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Effect of V_2O_5 on microwave dielectric properties of non-stoichiometric $MgTiO_3$ ceramics

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ABSTRACT

We report the effect of V_2O_5 addition on crystal structure, microstructure and microwave dielectric properties of non-stoichiometric $MgTiO_3$ ($Mg_{1+\delta}TiO_{3+\delta}$, where δ is excess MgO concentration) ceramics. The structural studies reveal that sample with $\delta = 0.07$ exhibits a single phase $MgTiO_3$ and secondary phase of $MgTi_2O_5$ (Mg_2TiO_4) for below (above) the $\delta = 0.07$ composition. The optimum microwave dielectric properties of $\varepsilon_r \sim 17.68$, $Q \times f_0 \sim 161$ THz at 9.4 GHz are obtained for $\delta = 0.07$, sintered at 1350 °C for 3 h. The improvement in loss is attributed to the improvement in uniform grain growth and suppression of secondary phases. V_2O_5 addition significantly lowered the sintering temperature of $Mg_{1.07}TiO_{3.07}$ to 1100 °C, which is due to the formation of liquid phase. The XRD analysis reveals that V_2O_5 forms a solid solution with MTO. A good combination of $\varepsilon_r \sim 15.8$ and $Q \times f_0$ of 85.6 THz at 9.3 GHz are obtained for 0.5 wt% V_2O_5 added $Mg_{1.07}TiO_{3.07}$.

1. Introduction

Recent days, due to rapid development in microwave communication technology, the microwave ceramics have been studied extensively. Microwave ceramics are used in various applications such as resonators, filters, oscillators and antennas in microwave communication devices. Furthermore, for the miniaturization of microwave devices, low-temperature co-fired ceramics (LTCC) have been widely investigated [1–4]. The components of the above microwave devices are made up of high dielectric constant (ε_r), low loss (high $Q \times f_0$) and a small temperature coefficient of resonant frequencies (τ_f) which are needed for enhanced functionality and better reliability [5]. However, most of the commercial microwave ceramics need very high sintering temperatures to enhance the density; this will increase the manufacturing cost. Also, Ag has been chosen as the conducting material to minimize the microwave absorption loss which melts around 980 °C. In order to use Ag as an electrode, the processing temperature of the microwave material needs to be brought down to this temperature range [6]. Generally, three different methods are used to reduce the sintering temperature of microwave ceramics; low-melting glassy additive [7], chemical methods [8] and smaller initial particle sizes [9]. Among the above techniques low-melting glassy additive is a cost-effective technique.

V_2O_5 is a well-known flux former at low temperatures and also acts as an oxygen donor, and hence it is chosen as a sintering aid [10]. Further, due to the hygroscopic nature of the MgO, it is difficult to synthesize the pure $MgTiO_3$ without additional phases Mg_2TiO_4 and $MgTi_2O_5$ by conventional solid-state reaction method [11]. Non-stoichiometric effect for various compounds has been reported by Belous et al. [12,13]. However, the influence of excess Mg on MTO ceramics to get a pure single phase and addition of V_2O_5 to the non-stoichiometric MTO has not been studied systematically. Hence, in the present study the non-stoichiometric $Mg_{1+\delta}TiO_{3+\delta}$ was prepared using conventional solid-state reaction method. The best composition which formed single phase $MgTiO_3$ was chosen and different wt% of V_2O_5 ($x = 0.0$–1.5 wt%) is added. The effect of V_2O_5 addition on crystal structure, microstructure and microwave dielectric properties of non-stoichiometric MTO ceramics is discussed. Furthermore, in both the cases, dielectric loss mechanisms were discussed, and the obtained results were compared with the earlier reports.

2. Experimental details

Samples with compositions $Mg_{1+\delta}TiO_{3+\delta}$ ($\delta = 0$, 0.05, 0.07, 0.10 and 0.15) in the magnesium titanate system were prepared using solid state reaction method. MgO (Sigma–Aldrich 99.99%) and TiO_2 (Sigma–Aldrich 99.99%, USA) compounds were used for

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preparation of these samples. The stoichiometry amounts of $Mg_{1+\delta}TiO_{3+\delta}$ compounds were weighed and mixed in a planetary ball mill (Fritsch GmbH, Germany) for 5 h using tungsten carbide vial and distilled water as milling medium. The prepared mixtures were dried and calcined at 1100 °C for 2 h. The calcined powders were re-milled for 10 h to reduce the particle size. The powders were added with an organic binder (PVA) and pressed into pellets with 10 mm in diameter and 4–5 mm in thickness under a pressure of 2000 kg/cm^2 isostatically. The pellets were subsequently sintered at 1200–1400 °C for 3 h in air.

From the above compounds, the best composition has been identified ($Mg_{1.07}TiO_{3.07}$) for further studies. After calcination $Mg_{1.07}TiO_{3.07}$ powders were re-milled with an inclusion of 0.5, 1.0 and 1.5 wt% of V_2O_5 (Sigma–Aldrich, USA) and pressed into pellets. The pellets were sintered in the temperature range of 1050–1200 °C for 3 h in air at a heating rate of 10 °C/min. A soak time of 30 min at 600 °C is given while heating to expel the binder. After sintering, the samples were cooled down to room temperature at a rate of 1 °C/min.

The phase purities of sintered $Mg_{1+\delta}TiO_{3+\delta}$ and V_2O_5 (x = 0.0–1.5 wt%) added ceramics were examined by recording the XRD patterns using X-ray diffractometer (Rigaku TTRAX-III) with CuK_α radiation (λ = 1.5406 Å). XRD patterns of 1.5 wt% V_2O_5 added $Mg_{1.07}TiO_{3.07}$ ceramics, sintered at different sintering temperatures were recorded using X-ray diffractometer (Seifert 3003 TT) with CuK_α radiation (λ = 1.5406 Å). The surface morphology of sintered samples was observed by scanning electron microscope (Leo 1430 vp) and chemical composition was studied with energy dispersive spectroscopy (EDS). The relative densities of the sintered specimens were measured by the Archimedes's method. The dielectric constant (ε_r) and quality factors (Q) of the samples at microwave frequencies were measured using the Hakki and Coleman dielectric resonator method, as modified and improved by Courtney [14,15]. Krupka resonant cavity oscillating in $TE_{01\delta}$ mode was connected with Vector Network Analyzer (VNA, Rohde & Schwarz, Model No.: ZVA24) has been used to measure the dielectric properties of the prepared ceramics.

3. Results and discussions

3.1. Crystal structure

Fig. 1(a) shows the X-ray diffraction patterns of excess mol concentration of MgO (δ = 0, 0.05, 0.07, 0.1 and 0.15) doped in $MgTiO_3$ ceramics sintered at 1350 °C. It is found that all the samples exhibited rhombohedral $MgTiO_3$ as a main crystalline phase (ICCD: 06-0464). For δ = 0 sample, along with $MgTiO_3$ a small amount of $MgTi_2O_5$ secondary phase is also observed. $MgTi_2O_5$ is usually formed as a secondary phase along with $MgTiO_3$, when prepared using solid-state reaction method [16].

The secondary phase peak intensity is suppressed with an increase in δ concentration and at a critical concentration of δ = 0.07 sample exhibiting a pure $MgTiO_3$ phase. With the increase in the δ beyond 0.07, a presence of Mg_2TiO_4 phase is observed along with $MgTiO_3$, and the intensity of Mg_2TiO_4 is improved with a further increase in δ. The magnified views of the secondary phase in XRD patterns are shown in Fig. 1(b). The presence of $MgTi_2O_5$ subordinate phase at δ = 0 may be due to the high hygroscopic nature of MgO, which absorbs moisture from the environment gives rise to deficiency in stoichiometry. From these results, one can conclude that excess MgO concentration plays a significant role on the formation of phase pure $MgTiO_3$ ceramics. Similar results were observed in the case of $MgTiO_3$ samples prepared from $MgCO_3.0.2708\ H_2O$ as initial powder [17]. Furthermore, the presence of $MgTi_2O_5$ ($\varepsilon_r \sim 17.4$, $Q \times f_0 \sim 47,000$ GHz, $\tau_f \sim -66$ ppm/°C) [18] and Mg_2TiO_4 ($\varepsilon_r \sim 14$, $Q \times f_0 \sim 150,000$ GHz, $\tau_f \sim -50$ ppm/°C) [19] are expected to influence the microwave dielectric properties of MTO ceramics significantly. The composition with δ = 0.07 is considered for the further study owing to the formation of phase pure MTO ceramics.

Table 1
Lattice parameters of $Mg_{1.07}TiO_{3.07} + x$ wt% of V_2O_5 obtained from the Reitveld refinement.

Composition in x (wt%)	$a = b$ (Å)	c (Å)
0.0	5.0539 (20)	13.8954 (15)
0.5	5.0539 (21)	13.8940 (29)
1.0	5.0535 (18)	13.8933 (27)
1.5	5.0533 (23)	13.8923 (32)

Table 2
The EDS spectra results of δ = 0 and δ = 0.15 doped $Mg_{1+\delta}TiO_{3+\delta}$ samples, sintered at 1350 °C.

Spot	Atom (%)		
	Mg (K)	Ti (K)	O (K)
For δ = 0			
A	19.94	19.84	60.23
B	12.71	23.93	64.51
For δ = 0.15			
A	17.48	19.48	60.61
B	28.33	14.21	57.46

Fig. 1(c) shows the XRD patterns of $Mg_{1.07}TiO_{3.07}$ (considered as a pure MTO with single phase for the addition of V_2O_5) composition added with different amounts of V_2O_5 (x = 0.0–1.5 wt%) sintered at 1100 °C for 3 h. It is observed that all the samples exhibited a rhombohedral $MgTiO_3$ phase without any secondary phase. To see the influence of V_2O_5 addition on crystal structure on $Mg_{1.07}TiO_{3.07}$ samples, all the samples are refined by considering a rhombohedral $R\bar{3}$ space group. The Rietveld refinement of $Mg_{1.07}TiO_{3.07}$ samples added with different wt% of V_2O_5 are shown in Fig. 2.

The lattice parameters are calculated and were summarized in Table 1. The lattice parameters are found to decrease with the addition of V_2O_5 addition, and this indicates that V_2O_5 forms a solid solution with $Mg_{1.07}TiO_{3.07}$. This can be explained as follows: V^{+5} can be substituted for tetravalent ions in $Mg_{1.07}TiO_{3.07}$, because the ionic radii of V^{5+} (0.54 Å) is smaller than Ti^{4+} (0.605 Å) in co-ordination number 6 [20,21]. Further, as the x wt% increases, the volume of the unit cell decreases, this shows that V^{5+} has entered into the MTO lattice. The XRD patterns of the 1.5 wt% V_2O_5 added $Mg_{1.07}TiO_{3.07}$, ceramics sintered at different sintering temperature is shown in Fig. 1(d). All the samples exhibit single phase $MgTiO_3$ phase and the formation of secondary phases is not observed with increasing sintering temperature up to 1150 °C.

3.2. Microstructure

The SEM images of $Mg_{1+\delta}TiO_{3+\delta}$ ceramics with different concentration of MgO (δ) doped samples sintered at 1350 °C are shown in Fig. 3. The sample revealed a porous and non - uniform microstructure for δ = 0 sample. Furthermore, small rods like grains are observed at grain boundary of larger grains, with an average grain size of 3.2 μm. An EDS analysis is performed to investigate the chemical composition of these grains, and the results were enlisted in Table 2. From the EDS spectra, the larger (spot A) and tiny grains (spot B) are confirmed as $MgTiO_3$ and $MgTi_2O_5$, respectively. Whereas a uniform grain growth and improved grain size are observed with an increase in δ up to δ = 0.07 (Fig. 3(b) and (c)). The average grain size of 9.1 and 10.2 μm is observed for δ = 0.05 and δ = 0.07 samples, respectively. Further, increase in MgO (i.e., δ = 0.15), porous grain morphology and two