Microwave Dielectric Properties of Zirconium Titanate Ceramics Doped with $MgNb_2O_6$

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Abstract

The sintering behaviour, microstructure and microwave dielectric properties of the $ZrTiO_4$ doped with $MgNb_2O_6$ were investigated systematically by X-ray diffractometry (XRD), scanning electron microscopy (SEM) and a network analyser at microwave frequencies. The XRD analysis confirmed a multi-phase orthorhombic α-PbO_2 type structure. The chosen composition, $0.67ZrTiO_4 - 0.33Mg_{1/3}Nb_{2/3}O_2$ (0.67ZT – 0.33MN), was sintered at 1400°C both in air and oxygen. The density improved significantly for the samples sintered in oxygen from 88% to 92%. Subsequently, the relative permittivity (ε_r) increased from 33 to 36 as the sintering atmosphere changed from air to oxygen. The quality factor increased from 27,500 GHz in air to 37,000 GHz in oxygen, while the temperature coefficient of resonant frequency (τ_f) for $0.67ZrTiO_4 - 0.33Mg_{1/3}Nb_{2/3}O_2$ was reduced to –12.4 ppm/°C, much lower than that for the end member $ZrTiO_4$ (+ 58 ppm/°C) and independent of sintering atmosphere.

Keywords: C. Dielectric Properties, D. TiO_2, ZrO_2, Niobates

Introduction

Low loss dielectric materials are of particular interest to wireless communication technology, mainly due to their use as the basis for resonators and filters. There are three essential characteristics of resonators in order to optimize the operability and viability of the commercial dielectric ceramics, and these are the dielectric constant (ε_r), the quality factor (Q), and the temperature coefficient of resonant frequency (τ_f).

The binary system ZrO_2 - TiO_2 has been studied extensively in last two decades because of its worldwide application the telecommunication industry. It was showed that the crystal structure of the single-phase $Zr_{1-x}Ti_{1+x}O_4$ ($0.0 \leq x \leq 0.167$) undergoes a sluggish order-disorder phase transformation on cooling below 1150°C. The high-temperature form has the α-PbO_2 – type structure, in which the tetravalent cations randomly occupy every octahedral site. Further studies by McHale and Roth on the crystal structure, as well as the composition of the low-temperature phase, showed an indication of triple *a*-axis and higher content of TiO_2. Therefore, this phase was identified as an ordered form of zirconium titanate having the same space group (*Pbcn*) and an ideal composition $ZrTi_2O_6$ (or $Zr_5Ti_7O_{24}$).

Based upon the microwave dielectric properties of $ZrTiO_4$ ($\varepsilon_r \approx 43$, $Q \times f \approx 22{,}000$ GHz and $\tau_f \approx +58$ ppm/°C at 1400°C it is necessary, for possible applications in dielectric resonators, that these parameters are optimised. In order to modify the τ_f, the binary niobate ceramics, with the formula ANb_2O_6 where A is a divalent cation (Ca, Zn, Mg, Co) and isostructural with the orthorhombic mineral columbite and highly negative τ_f, were chosen for this study. Most niobate columbites sinter between 1100-1300°C, much lower than that for the zirconium titanate and the niobates possess a much higher quality factor. Recent studies by Lee et al. showed

that $MgNb_2O_6$, in particular, exhibit excellent dielectric properties; $\varepsilon_r \approx 18.4$, $Q \times f \approx$ 93,800 GHz and $\tau_f \approx$ -70 ppm/°C.

Experimental

The starting powders, ZrO_2 (Magnesium Electron, Mel E101), TiO_2 (Alfa Aesar, Rutile 99.8%), MgO (Alfa Aesar , 99.95%) and Nb_2O_5 (H.C. Stark) were mixed using solid-state reaction to yield the composition $0.67ZrTiO_4 - 0.33Mg_{1/3}Nb_{2/3}O_2$ (0.67ZT – 0.33MN). It was calcined at 900ºC for 4hrs and pressed into cylindrical shaped pellets. Sintering was undertaken in a closed tube furnace (Vecstar, Model VTFSP/1500°C) in oxygen and air at 1400ºC for 4 hrs. Product densities were determined from weight and dimension measurements. Average grain sizes were determined by the linear intercept method.

Phase identification and crystal structure analysis of polished products were undertaken using a Philips X'PERT X-ray diffraction system (PW 3710) over the 2θ range 20° to 80° with a step size of 0.04º. Before analysis, all sintered specimens were ground using 1200 grade SiC and subsequently polished on 6μm, 1μm and 0.25μm diamond paste followed by OPS (colloidal Silica suspension). The microstructures of the as-sintered and polished specimens were examined by scanning electron microscopy (XL30 FEG-SEM). Wave length dispersion spectroscopy (WDS, Cameca Electron Probe Microscope SX100) was used for the quantative chemical analysis of the samples.

The microwave dielectric properties (relative permittivity and dielectric Q value) were determined at 3.5 GHz by the Hakki and Coleman method, from the resonant frequency and the peak width of the TE_{011} resonant mode. The temperature coefficient

of resonant frequency (τ_f) was determined by a cavity method over the temperature range -20^{o}C to +60^{o}C.

Results

Figure 1 shows typical X-ray diffraction spectra of the 0.67ZT – 0.33MN system in oxygen at 1400°C. All the reflections could be indexed satisfactorily in the orthorhombic α-PbO_2 cell (space group *Pbcn*). Second-phase was also detected by adding 0.33 mol% $MgNb_2O_6$ to $ZrTiO_4$. The CELREF software was used to determine the lattice parameters of the compound. The results showed no variation with sintering atmosphere. Therefore the following results could be reported for the cell parameters: a = 4.7850, b = 5.5298 and c = 5.0439 Å. The microstructure of the as-sintered surface confirmed the formation a homogenous and uniform matrix along with small second-phase grains. (Figure 2) The backscattered electron image of the polished surface of 0.67ZT – 0.33MN, showed clearly the formation of the second-phase, indicated that the composition to be equivalent to $MgTi_{1.6}Nb_{0.2}Zr_{0.2}O_5$ based on Wavelength Dispersive Spectrometry (WDS) results. (Figure 3)

Table 1 shows the results for the relative permittivity and the quality factor as a function of atmosphere. It can be seen that the dielectric properties improved considerably after sintering in oxygen as a result of the improved sinterability as well as the prevention of tetravalent elements such as Ti^{+4} from reduction in air. The reduction of tetravalent cations usually leads to the formation of the electronic defects (introduction of oxygen vacancies), followed by darkened interior. As the bulk density of $0.67ZrTiO_4 – 0.33Mg_{1/3}Nb_{2/3}O_2$ ceramics increases by firing the samples in oxygen, the result appears slightly beneficial for the improvement of the dielectric

constant. Due to the lower permittivity of the magnesium niobate the overall permittivity of the system is much lower than the end member $ZrTiO_4$.

The quality factor is supposed to be influenced by defect concentrations such as oxygen vacancies, second phases, grain size and density/porosity. According to Iddles et al. the Q-values are independent of density or porosity for samples with relative densities in the range of 90 – 98%. Therefore, the improved quality factor for samples sintered in oxygen could be as a result of the improved density (less pores) and subsequently presence of less lossy regions in the matrix. Further investigation by Iddles et al. on ZrO_2 -TiO_2-SnO_2 ceramics doped with either La_2O_3 or Nb_2O_5 showed that the grain size increased with sintering time but the change was independent for Q-value. Moreover there is no published report proposing the dependence of Q on grain size in any type of microwave ceramics.

Addition of 0.33 mol% $MgNb_2O_6$ seems to increase the overall Q-value as well as the τ_f of the zirconium titanate due to the formation of the titanium-rich phase. The temperature coefficient of resonant frequency of the $0.67ZrTiO_4 – 0.33Mg_{1/3}Nb_{2/3}O_2$ system could be modified to –12.4 ppm/°C. Further studies are under investigation to adjust the τ_f to zero for practical applications.

Conclusions

The phase relationship and microwave dielectric properties of the $0.67ZrTiO_4 – 0.33Mg_{1/3}Nb_{2/3}O_2$ system was investigated. The ZT – ZN system is based on the α -PbO_2 structure. A rich-titania phase was formed from the matrix with a composition equivalent to $MgTi_{1.6}Nb_{0.2}Zr_{0.2}O_5$. With 0.33 mol% $MgNb_2O_6$ addition, a dielectric

constant of 35, Q×f value of 37,000 GHz and a τ_f value of –12.4 ppm/°C were obtained for $ZrTiO_4$ – $MgNb_2O_6$ ceramics sintered at in oxygen.

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Figure 1: Typical XRD spectra for $0.2Mg_{1/3}Nb_{2/3}O_2$ – $0.4ZrTiO_4$ sintered in oxygen for 4 hours at 1400°C.

Figure 2: SEM (Left) and Back scattered (Right) micrographs of as-sintered surfaces of $0.2Mg_{1/3}Nb_{2/3}O_2$ – $0.4ZrTiO_4$ system (a, b) Air, (c, d) Oxygen

Figure 3: Back scattered micrograph of the polished surface of $0.2Mg_{1/3}Nb_{2/3}O_2$ – $0.4ZrTiO_4$ system.

Table 1: Microwave Dielectric properties of the $0.2Mg_{1/3}Nb_{2/3}O_2 - 0.4ZrTiO_4$ ceramics.

$0.2Mg_{1/3}Nb_{2/3}O_2 - 0.4ZrTiO_4$	Bulk Density [g/cm^3]	ε_r	Q×f [GHz]	τ_f (ppm/°C)
Oxygen	4.46	35	37,000	-12.4
Air	4.65	33	27,500	-12.7

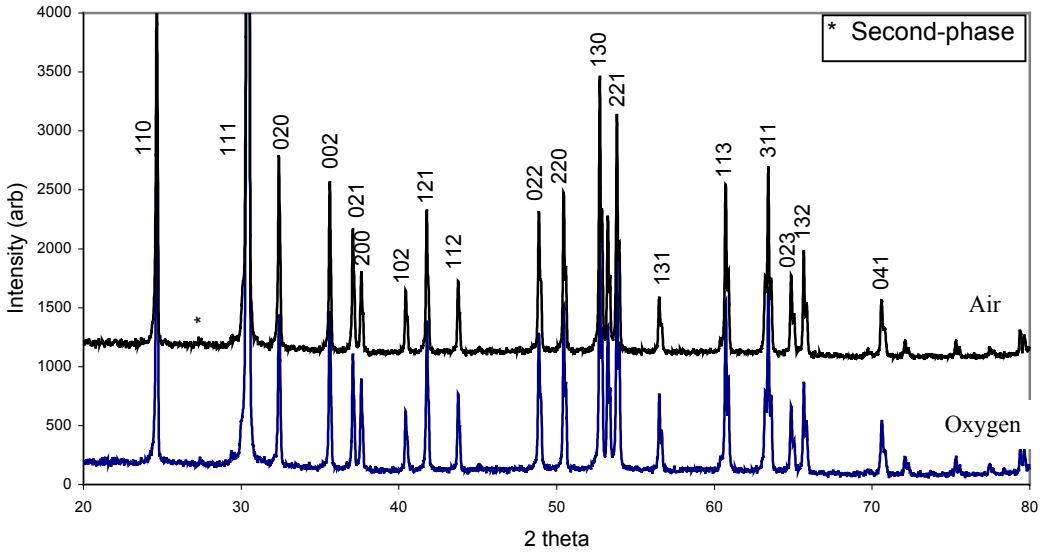
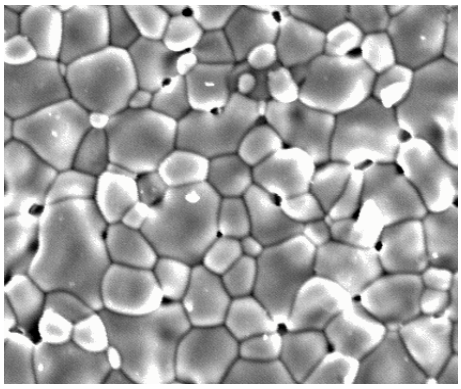
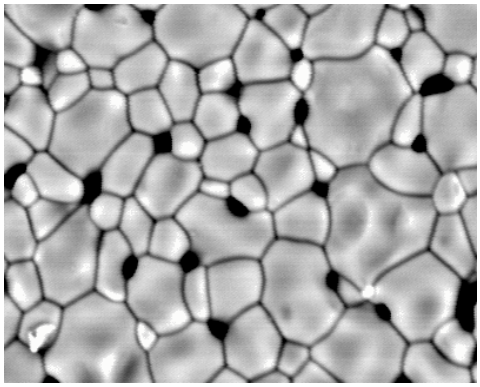


Figure 1



(a)



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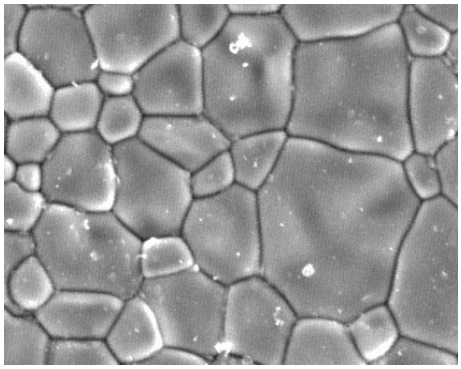
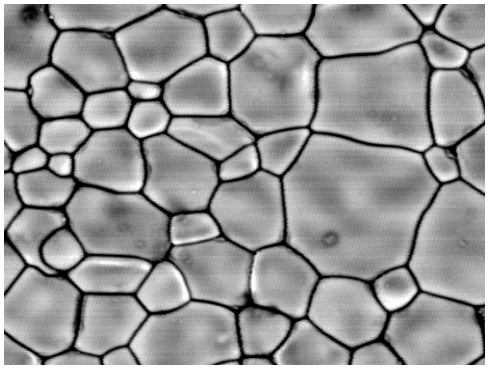


(c)



(d)

Figure 2

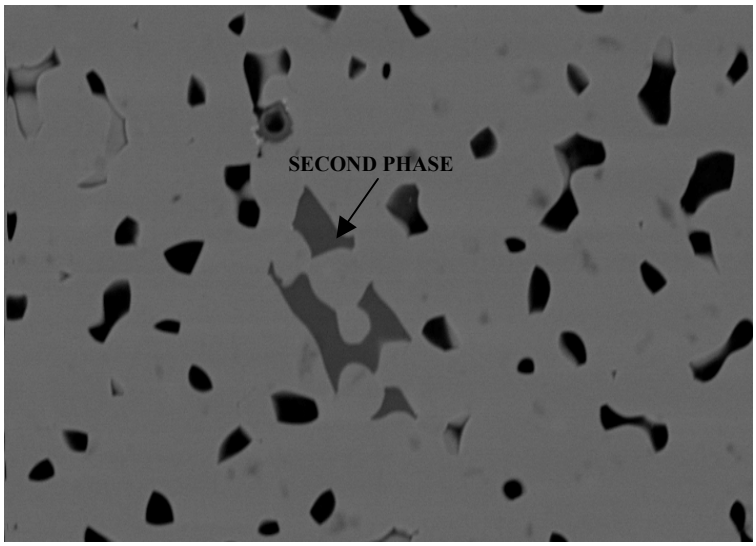


Figure 3