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ScienceDirect

Ceramics International 42 (2016) 7681–7689

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Relationship of the structural phase transition and microwave dielectric properties in $MgZrNb_2O_8$–TiO_2 ceramics

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Received 21 January 2016; received in revised form 27 January 2016; accepted 27 January 2016
Available online 1 February 2016

Abstract

The phase transition, microstructure and microwave dielectric properties were systematically investigated in TiO_2 modified $MgZrNb_2O_8$ ceramics. The X-ray diffraction and Raman spectrum revealed four distinct phase regions from wolframite, ixiolite, ixiolite–rutile mixture to rutile with increasing the TiO_2 content. This phase transition was considered as a result of the destruction of the ordered array of octahedra in wolframite structure and then the shortening of cation–cation distances in ixiolite structure. Moreover, the addition of TiO_2 was found to improve the sintering behavior of the $MgZrNb_2O_8$ ceramics and simultaneously promote grain growth. The microwave dielectric properties were found to be closely related to the phase transition, packing fraction, Raman shift and full width at half-maximum of A_{1g} stretch mode. A near-zero temperature coefficient of the resonant frequency could be achieved together with a middle dielectric permittivity of $\varepsilon_r \sim 43$ and a relatively high $Q \times f$ value of 46,110 GHz for the $0.63MgZrNb_2O_8$–$0.37TiO_2$ samples sintered at 1300 °C for 4 h.

Keywords: A. Sintering; B. X-ray methods; C. Dielectric properties

1. Introduction

Microwave dielectric ceramics are of much interest as they own high relative permittivity ε_r, high quality factor $Q \times f$, near-zero temperature coefficient of the resonant frequency τ_f, low cost of raw materials, low processing temperature, and low bulk density [1–3]. However, it is a rather difficult task to achieve all these requirements in one material. An alternative solution would be then to reach a compromise over these properties.

Columbite-structured niobates ANb_2O_6 (A=Mg, Mn, Co, Ni, and Zn) have been extensively investigated as candidate materials for dielectric resonators in base station of telecommunication system [4–6]. Another type of niobates, $AZrNb_2O_8$ (A=Mn, Mg, Zn and Co) ceramics with a monoclinic wolframite structure have also been reported to possess excellent microwave dielectric properties [7]. Among them, $MgZrNb_2O_8$ is one of the most promising compositions because of its highest $Q \times f$ value previously reported (ε_r=26, $Q \times f$=120,816 GHz, and τ_f= −50.2 ppm/°C) [8]. It could be applicable in some microelectronic technologies such as microwave integrated circuit substrates and gate dielectrics if its negative τ_f value can be tailored to be near zero. To the best of our knowledge, rutile TiO_2 is a very popular compound with a positive τ_f value (+465 ppm/°C) and has been commonly used as a τ_f tailor for a good temperature stability [9,10]. The phase structure and microwave dielectric properties were found to be correlated in TiO_2 modified $ZnNb_2O_6$ ceramics due to similar structures between columbite and rutile phases [2,11,12]. In fact, the above-mentioned structures such as columbite, wolframite, ixiolite and rutile, are all closely related to an α-PbO_2 typed structure. It consists of close-packed oxygen layers, in which cations occupy one-half of the octahedral voids [13]. Thus, the structural homology between wolframite $MgZrNb_2O_8$ and rutile TiO_2 encouraged us in this work to explore whether and/or how a close relationship between the structure and property exists in $MgZrNb_2O_8$–TiO_2 (x=0–1, in volume fraction) ceramics.

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http://dx.doi.org/10.1016/j.ceramint.2016.01.182
0272-8842/

2. Experimental procedure

The starting materials used were high-purity powders of analytic-grade $(MgCO_3)_4 \cdot Mg(OH)_2 \cdot 5H_2O$, ZrO_2, Nb_2O_5 (Sinopharm Chemical Reagent Co. Ltd, Shanghai, China) and TiO_2 (Xilong Chemicals, Guangdong, China). The $MgZrNb_2O_8$ powder with a stoichiometric composition was first synthesized using a conventional solid-state reaction route. The calcination was carried out at 1200 °C for 4 h. The $(1-x)MgZrNb_2O_8$–$xTiO_2$ composite powders were weighed in appropriate proportions and subsequently ball milled in a nylon jar using zirconia balls and alcohol as media on a planetary milling machine (QM-3SP2, Nan Da Instrument Plant, Nanjing, China). After drying, the powder mixture was granulated with 5 wt% PVA as a binder, and then pressed into cylinders of 10 mm in diameter and 5–6 mm in height under a uniaxial pressure of 100 MPa. These samples were first heated at 550 °C for 4 h to burn out the organic binder, and then sintered in air in the temperature range of 1260 °C to 1340 °C for 4 h.

The bulk densities of the sintered samples were measured by the Archimedes method. The crystalline structure of the sintered samples was determined by an X-ray diffractometer (XRD, D/Max2500V, Rigaku, Tokyo, Japan) using Cu $K\alpha$ radiation ($\lambda = 1.5406$ Å) with a step size of 0.01°. The structural parameters were obtained from the Rietveld refinement of the XRD data using the Fullprof software. The microstructural observation of the post-sintered pellets and the quantitative analysis of elements in different grains were performed using a scanning electron microscope (SEM, JEOL JSM-6490LV, Tokyo, Japan) equipped with an energy dispersive spectrometer (EDS). Raman spectrum was collected at room temperature using a Raman spectrometer (633 nm, LabRAM HR800, HJY, Longjumeau Cedex, France). A network analyzer (Agilent, N5230C, Palo Alto, CA) and a temperature chamber (GDW-100, Saiweisi, Changzhou, China) were used to measure the dielectric properties of the well-polished ceramic samples with an aspect ratio of 1.8–2.2 by means of a Hakki–Coleman post-resonator method [14]. The dielectric permittivity ε_r was measured using two parallel conducting plates and two coaxial electric probes as suggested by Courtney at the TE_{011} mode of resonance, which can be least perturbed by the surrounding field variations [15]. For the measurement of the Q value, the sample was placed on a low-loss quartz support of 8 mm diameter and 4 mm height in the center of the silver-clad cylindrical shielded cavity (Resonant cavity, QWED, Warsaw, Poland). The loaded quality factor Q_L in transmission mode (S_{21} parameter) was determined from the full width of the resonance peak at the 3 dB level. The dielectric loss ($\tan\delta$) was calculated by using the software provided by the $TE_{01\delta}$-shield cavity supplier, through which the Q values can be obtained in accordance with the equation $Q = 1/\tan\delta$. The τ_f value of the samples was measured by noting the change in the resonant frequency over a temperature interval from 25 °C to 80 °C, as calculated by the following equation:

$$\tau_f = \frac{f_2 - f_1}{f_1(T_2 - T_1)} \quad (1)$$

where f_1 and f_2 represent the resonant frequencies at T_1 and T_2, respectively.

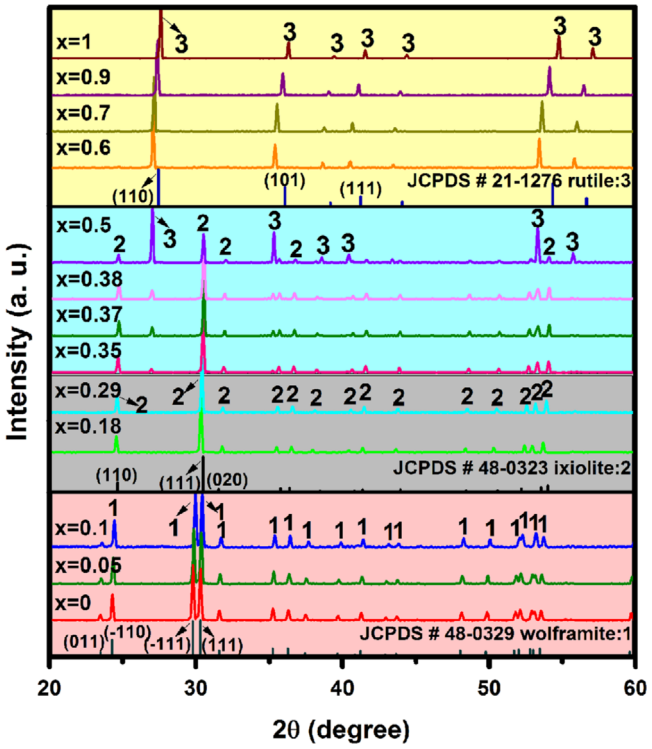

Fig. 1. XRD patterns of $(1-x)MgZrNb_2O_8$–$xTiO_2$ ($x = 0$–1) ceramics sintered at 1300 °C for 4 h. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

3. Results

Fig. 1 shows XRD patterns of $(1-x)MgZrNb_2O_8$–$xTiO_2$ ($x = 0$–1) ceramics. With increasing the TiO_2 content, the ceramics were found to experience four phase regions in sequence: wolframite → ixiolite → ixiolite + rutile → rutile. When the TiO_2 content was less than 0.10, a wolframite solid solution was formed (magenta region), which could be well indexed to the pattern of $MgZrNb_2O_8$ (JCPDS 48-0329) with a space group of $P2/c$ ($C2h$). As the TiO_2 content was further increased, only an ixiolite phase existed within $0.18 \le x \le 0.29$ (gray region), implying there is a phase transition from a monoclinic wolframite phase to an orthorhombic ixiolite phase in the composition range of $0.1 < x < 0.18$. The diffraction peaks of the ixiolite phase matched well with the standard diffraction pattern of $ZnTiNb_2O_8$ (JCPDS 48-0323) with a space group $Pbcn$ ($D2h$). As $0.35 \le x \le 0.5$, the (110), (101) and (111) diffraction lines of rutile TiO_2 started to appear and their intensities gradually increased, illustrating that a diphasic region (cyan region) was formed due to the limited solubility of Ti^{4+} in the previous ixiolite solid solution. As the TiO_2 content exceeded 50 vol%, the ixiolite phase faded away and a rutile-type ($P42/mnm$, $D4h$) solid solution (yellow region) appeared, which could be well indexed to the pattern of TiO_2 (JCPDS 21-1276). Besides the multiple phase transition, the diffraction peaks of all phases shifted toward higher angles with increasing the TiO_2 content, indicating that the unit cell volumes of the ceramics decreased in the entire composition range.

To study the structure characteristics in more detail, Rietveld refinement was carried out using the Fullprof program on the