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Journal of the European Ceramic Society 32 (2012) 3287–3295
www.elsevier.com/locate/jeurceramsoc

High-Q dielectrics using ZnO-modified Li_2TiO_3 ceramics for microwave applications

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Received 5 December 2011; received in revised form 20 March 2012; accepted 20 March 2012
Available online 16 April 2012

Abstract

The microwave dielectric properties of the $(1-x)Li_2TiO_3$–xZnO ($x=0.1$–0.5) ceramic system prepared by mixed oxide route have been investigated. The rock-salt structured $(1-x)Li_2TiO_3$–xZnO were characterized by using X-ray diffraction spectra, scanning electron microcopy (SEM). The dielectric properties are strongly dependent on the compositions, the densifications and the microstructures of the specimens. The decrease of $Q\times f$ value at high-level ZnO addition ($x>0.3$) was owing to the intensity of the (0 0 2) superstructure reflection decreased and became disordered rock-salt structure. For practical applications, a new microwave dielectric material $0.7Li_2TiO_3$–0.3ZnO is suggested and it possesses a good combination of dielectric properties with an ε_r of ~22.95, a $Q\times f$ of ~99,800 GHz (measured at 8.91 GHz), and a τ_f of ~0 ppm/°C. A low-loss dielectric resonant antenna using aperture-coupled cylindrical dielectric resonant was designed and fabricated using the proposed dielectric to study its performance.

Keywords: Powders-solid state reaction; Composites; Electron microscopy; X-ray methods; Dielectric properties

1. Introduction

The development of microwave dielectric materials for applications as substrates, resonators, filters, and patch antennas in communication systems has received much more attention in the last two decades. A material with a high dielectric constant for volume efficiency is a major requirement in modern wireless communication technology. In addition, a low-dielectric-loss for better selectivity and a near-zero temperature coefficient of resonant frequency (τ_f) for stable frequency stability is also critical requirements for practical applications.[1,2] Dielectric materials subject to these requirements have been reported for microwave and millimeter wave applications and research on new microwave dielectrics is still ongoing and has become a primary issue in the last few years.[3–15]

Ternary rock-salt oxide ceramic system $A_aB_bO_{a+b}$ (where $A^+=$Li, Na; $B^{4+}=$Ti, Sn, Zr; $B^{5+}=$Nb and Ta) have been reported due to their excellent microwave dielectric properties.[16–20] Lithium titanium (Li_2TiO_3), one of the rock-salt type ceramics with a general formula of A_2BO_3, undergoes an order-disorder phase transition at 1213 °C, and having a high melting point at 1547 °C.[21] Moreover, it also possesses a high-dielectric-constant (ε_r~22.0), a high quality factor ($Q\times f$~63,500 GHz) and positive τ_f value (20.3 ppm/°C).[16] In the Li_2TiO_3–MgO ceramic system, it formed complete solid solution with MgO and order-disorder phase transition with increasing MgO content. Solid solution compositions may also be written as $Li_{2/3(1-x)}Ti_{1/3(1-x)}Mg_xO$ proposed by Castellanos and West[21] In addition, the $(1-x)Li_2TiO_3$–xMgO solid solution replacement mechanism could be proposed as $2Li^++Ti^{4+}\leftrightarrow 3Mg^{2+}$, where charge balance was maintained.[22] When $x=0.24$, an excellent combination of microwave dielectric properties ($\varepsilon_r=19.2$, $Q\times f=106{,}226$ GHz, and a $\tau_f=3.56$ ppm/°C) can be obtained.

In the present work, an inexpensive, easy to process ceramic system is proposed for applications in today's HIPERLAN (high-performance radio local area network, 5150–5350 MHz) antennas. The $(1-x)Li_2TiO_3$–xZnO solid solution (can be written as $Li_{2(1-x)}Ti_{(1-x)}Zn_xO_{(3-2x)}$) was synthesized to investigate its microwave dielectric properties because the ionic radii of Zn^{2+} (0.74 Å, CN = 6)[23] are similar to that of Li^+ (0.76 Å, CN = 6)[23] and Ti^{4+} (0.605 Å, CN = 6).[23] The resultant

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0955-2219/$ – see front matter
http://dx.doi.org/10.1016/j.jeurceramsoc.2012.03.030

microwave dielectric properties analysis were based on the densification, X-ray diffraction (XRD) patterns, and microstructures of the ceramics. The correlation between the microstructure and the $Q \times f$ value was also investigated.

2. Experimental procedure

Sample of Li_2TiO_3 was synthesized by conventional solid-state methods from individual high-purity oxide powders (99.9%): Li_2CO_3 and TiO_2. The initial oxide powders were mixed and ground in an agate ball mill together with distilled water for 24 h. The wet mixtures were dried at 100 °C, thoroughly milled before they were calcined 800 °C for 2 h. The calcined powders were mixed according to the molar fraction $(1-x)Li_2TiO_3$–xZnO (x = 0.1–0.5). The fine powder with 3 wt% of a 10% solution of PVA as a binder (Polyvinyl alcohol 500, Showa, Japan), granulated by sieving through 200 mesh, and pressed into pellets with 11 mm in diameter and 5 mm in thickness. All samples were prepared using an automatic uniaxial hydraulic press at 2000 kg/cm^2. These pellets were sintered at temperatures of 1120–1300 °C for 2 h in air. The heating rate and the cooling rate were both set at 10 °C/min.

The crystal phases of the sintered ceramics were identified by XRD using Cu$K\alpha$ (λ = 0.15406 nm) radiation with a Siemens D5000 diffractometer (Munich, Germany) operated at 40 kV and 40 mA. The microstructural observations and analysis of the thermal-etched surfaces were performed by scanning electron microscopy (SEM; Philips XL-40FEG, Eindhoven, the Netherlands) and an energy-dispersive X-ray spectrometer (EDS, Philips). The apparent densities of the sintered pellets were measured by the commonly the Archimedes method. The theoretical densities of the $(1-x)Li_2TiO_3$–xZnO solid solution could be calculated from the lattice parameters. Therefore, the relative density can be obtained by taking the ratio of apparent density/theoretical density. The dielectric constant (ε_r) and the quality factor values (Q) at microwave frequencies were measured using the Hakki–Coleman dielectric resonator method.[24,25] A system combining an HP8757D network analyzer (HP, Palo Alto, CA) and an HP8350B sweep oscillator (HP, Palo Alto, CA) was employed in the measurement. For temperature coefficient of resonant frequency (τ_f), the technique is the same as that of quality factor measurement. The test cavity was placed over a thermostat in the temperature range of 25–80 °C. The τ_f value (ppm/°C) was calculated by noting the change in resonant frequency (Δf)

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

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

A low-loss dielectric resonant (hereafter referred to as DR) antenna using aperture-coupled cylindrical DR fed with microstrip line was designed and measured through PNA series network analyzer (E8364A). According to Long et al.,[26] the resonant frequency (f_r) of circular DR antenna excited at the dominant $TM_{11\delta}$ mode was can be approximated by

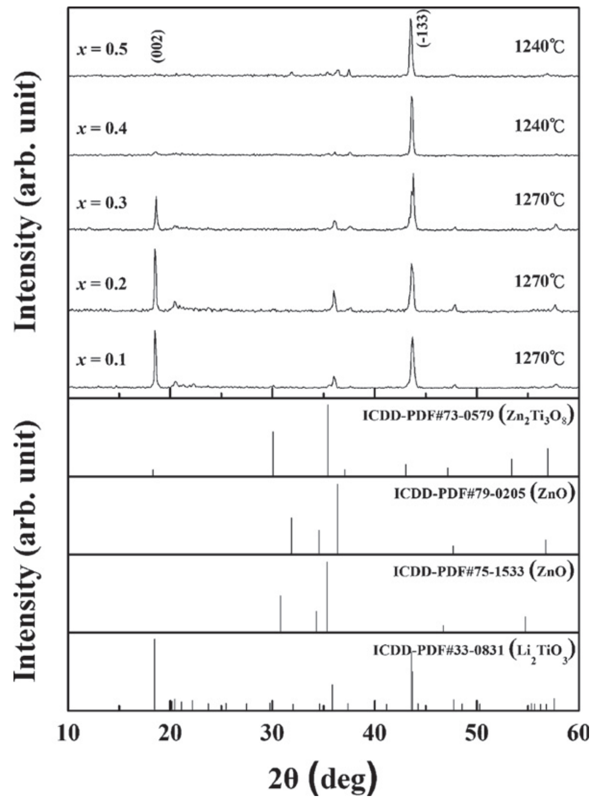

Fig. 1. X-ray diffraction patterns of $(1-x)Li_2TiO_3$–xZnO (x = 0.1–0.5) ceramic system sintered at different sintering temperatures for 2 h.

$$f_r = \frac{c}{2\pi\sqrt{\varepsilon_r}}\sqrt{\left(\frac{X'_{11}}{a}\right)^2 + \left(\frac{\pi}{2h}\right)^2} \tag{2}$$

where c is the speed of light in vacuum and $X'_{11} = 1.841$ is the fist zero of the equation $J'_1(x) = 0$.

The parameters of ε_r, a and h is the permittivity, radius and height of the DR antenna, respectively. This work proposes a low-loss dielectric resonant antenna design for application in the 5.2 GHz licensed band of HIPERLAN system.

3. Results and discussion

Fig. 1 illustrates the room temperature XRD patterns recorded from the $(1-x)Li_2TiO_3$–xZnO ceramic system sintered at different temperatures for 2 h. A rock-salt monoclinic phase of Li_2TiO_3 type (ICDD-PDF#00-033-0831), belonging to the space group C2/c (15), was identified as the main phase implying a forming of solid solution. Additional phase formation was not detected throughout the complete range of mixtures under test. However, some ZnO and $Zn_2Ti_3O_8$ were identified for specimen with x = 0.5, which might be attributed to an excess ZnO content or out of solubility. With increasing ZnO content, the intensity of the (0 0 2) superstructure reflection decreased and became a disordered rock-salt structure at x = 0.4, suggesting it undergoes an order-disorder phase transition. Solid solution compositions may also be written as $Li_{2(1-x)}Ti_{(1-x)}Zn_xO_{(3-2x)}$.