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Microwave dielectric properties of novel temperature stable high Q $Li_2Mg_{1-x}Zn_xTi_3O_8$ and $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn) ceramics

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Abstract

The $Li_2Mg_{1-x}Zn_xTi_3O_8$ ($x = 0$–1) and $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn and $x = 0$–0.2) ceramics are synthesized by solid-state ceramic route and the microwave dielectric properties are investigated. The $Li_2MgTi_3O_8$ ceramic shows $\varepsilon_r = 27.2$, $Q_u \times f = 42{,}000$ GHz, and $\tau_f = (+)3.2$ ppm/°C and $Li_2ZnTi_3O_8$ has $\varepsilon_r = 25.6$, $Q_u \times f = 72{,}000$ GHz, and $\tau_f = (-)11.2$ ppm/°C respectively when sintered at 1075 °C/4 h. The $Li_2Mg_{0.9}Zn_{0.1}Ti_3O_8$ dielectric ceramic composition shows the best dielectric properties with $\varepsilon_r = 27$, $Q_u \times f = 62{,}000$ GHz, and $\tau_f = (+)1.1$ ppm/°C. The effect of Ca substitution on the structure, microstructure and microwave dielectric properties of $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn and $x = 0$–0.2) has also been investigated. The materials reported in this paper are excellent in terms of dielectric properties and cost of production compared to commercially available high Q dielectric resonators.

Keywords: Microwave dielectrics; Resonator; LMT; LZT

1. Introduction

In pace with the advances in microwave telecommunication and satellite broadcasting, a variety of microwave devices have been developed using dielectric resonators and the resonators have become indispensable components in microwave communication systems.[1–4] The microwave dielectric materials are advantageous in terms of compactness, light weight, temperature stability and low cost in the production of high frequency devices.[5,6] The current trend and the state of the art of microwave dielectric materials for telecommunication applications are discussed in a recent book "Dielectric materials for wireless communications".[4] The complex perovskites such as $Ba(Zn_{1/3}Ta_{2/3})O_3$ (BZT) and $Ba(Mg_{1/3}Ta_{2/3})O_3$ (BMT) show the highest quality factor ($Q \times f > 150{,}000$) with low τ_f.[7–9] However, they are made up of expensive chemicals such as tantalates or niobates. The $(Zr_{1-x}Sn_x)TiO_4$, $Ba_2Ti_9O_{20}$, $BaTi_4O_9$ are some low cost materials which show useful microwave dielectric properties.[10–12] However, high sintering temperature together with a long annealing time is necessary for obtaining excellent microwave dielectric properties. Hence, these high Q dielectric ceramics are not cost effective either in terms of its cost of raw materials or its high processing temperature. A variety of microwave devices have been developed using dielectric resonators as the frequency determining components. However, due to the constraints of size, frequency of operation, frequency stability and selectivity, only those materials with high relative permittivity (ε_r), low dielectric loss and nearly zero temperature coefficient of resonant frequency (τ_f) can meet the requirements for DR applications.[1,3,4,13,14] Another constraint in making light weight electronic modules is the high density (≈ 5 g/cm^3) of dielectric ceramics and the cost of production. These requirements put constraints on the number of materials available for DR applications. The reported dielectric materials in the literature so far have failed either atleast one of its important properties such as cost of the raw materials, sintering temperature, permittivity, quality factor, temperature coefficient of resonant frequency, or bulk density. Achieving all these requirements in one material is a formidable task and optimal balance of these properties is one of the major challenges in the electronic industry. Recently West et al. reported the crystal structure of ternary spinal such as $Li_2MgTi_3O_8$ and $Li_2ZnTi_3O_8$ ceramics.[15,16] However, their electrical properties have not been reported so far.

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This paper discusses the synthesis, characterization and microwave dielectric properties of novel low loss dielectric materials ($Li_2Mg_{1-x}Zn_xTi_3O_8$ ($x = 0$–1) and $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn and $x = 0$–0.2)) having spinel structure which satisfies all the above mentioned requirements and can address the growing demand of microelectronic industry.

2. Experimental

The $Li_2Mg_{1-x}Zn_xTi_3O_8$ ($x = 0$–1) and $Li_2A_{1-x}Ca_xTi_3O_8$ (A = Mg, Zn and $x = 0$–0.2) ceramic samples were prepared by the conventional solid-state ceramic route. High purity Li_2CO_3, ZnO, $(MgCO_3)_4$ $Mg(OH)_2$ $5H_2O$, $CaCO_3$ and TiO_2 (99.9+%, Aldrich Chemical Company, Inc., Milwaukee, WI, USA) were used as the starting materials. Stoichiometric amounts of the powder samples were mixed and ball milled using zirconia balls in ethanol medium for 24 h. The resultant slurry was then dried and calcined at 900 °C/4 h. The calcined powders were ground to form fine powders and polyvinyl alcohol (PVA) (molecular weight 72,000, BDH Lab Suppliers, England) solution was then added to the powder, mixed, dried and ground well and pressed into cylindrical disks of about 14 mm diameter and 7 mm thickness, by applying a pressure of about 100 MPa. These compacts were muffled by powder of the same composition and sintered at different temperatures in the range 1000–1125 °C/4 h. The sintering temperature was optimized for the best density and dielectric properties. The crystal structure and phase purity of the powdered samples were studied by X- ray diffraction technique using Ni-filtered Cu-Kα radiation using Rigaku Dmax-I, Japan, diffractometer. The microstructures of the sintered samples were studied using scanning electron microscope (JEOL-JSM 5600 LV, Tokyo, Japan). The sintered density of the specimen was measured by the Archimedes method. The microwave dielectric properties were measured in the frequency range 4–6 GHz by a Vector Network Analyzer (8753 ET, Agilent Technologies). The dielectric constant and unloaded quality factor of the samples were measured by Hakki and Coleman and cavity methods respectively.[4,17,18]

3. Results and discussion

3.1. Phase analysis and the microwave dielectric properties of $Li_2Mg_{1-x}Zn_xTi_3O_8$ ceramics

Fig. 1 shows the variation of the relative density of $Li_2MgTi_3O_8$ (LMT) and $Li_2ZnTi_3O_8$ (LZT) ceramics calcined at 900 °C/4 h as a function of sintering temperature. As the sintering temperature increased to 1075 °C/4 h, the relative density increased to a maximum value and further increase in sintering temperature decreased the density. The improvement in densification could be due to the elimination of pores in the ceramics. A maximum densification of 95.5% and 95% is observed for LMT and LZT ceramics respectively at a sintering temperature of 1075 °C/4 h. It is reported that lithium is volatile and escapes at high sintering temperatures.[19,20] The decreased densification at higher sintering temperature could be due to the trapped porosity by the evaporation of lithium and also due to the abnormal grain growth.

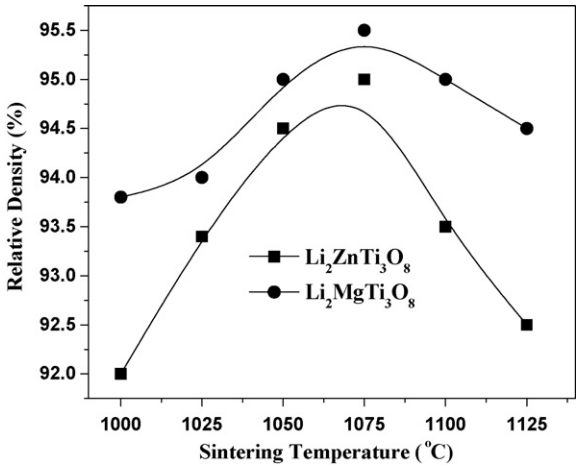

Fig. 1. Variation of relative density of (a) $Li_2MgTi_3O_8$ and (b) $Li_2ZnTi_3O_8$ ceramics as a function of sintering temperature.

Fig. 2 shows the X-ray diffraction pattern of $Li_2Mg_{1-x}Zn_xTi_3O_8$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1) ceramics sintered at its optimized sintering temperature of 1075 °C/4 h. All the peaks are indexed based on JCPDS file number 48-0263 for $Li_2MgTi_3O_8$ and 86-1512 for $Li_2ZnTi_3O_8$ with cubic crystal symmetry. The strongest peak is observed at $2\theta = 18.2995$ ($d = 4.8442$) for $Li_2MgTi_3O_8$ and $2\theta = 35.526$ ($d = 2.52488$) for $Li_2ZnTi_3O_8$ respectively. As x increases in $Li_2Mg_{1-x}Zn_xTi_3O_8$ ceramics, a sudden shift of strongest intensity peak from $2\theta = 18.2995$ to 35.526 is observed. This shift is observed near $x = 0.1$. As x increases, the cell parameter and the cell volume of $Li_2Mg_{1-x}Zn_xTi_3O_8$ decrease as shown in Fig. 3. The lattice parameter is $a = 8.381(4)$ Å for $Li_2MgTi_3O_8$ and $a = 8.372(2)$ Å for $Li_2ZnTi_3O_8$ which is consistent with corresponding reported JCPDS files. The $Li_2Mg_{1-x}Zn_xTi_3O_8$ ceramic has a cubic symmetry and the lattice parameter is calculated by plotting 'a' versus $\sin^2(\theta)$.[21] A straight line

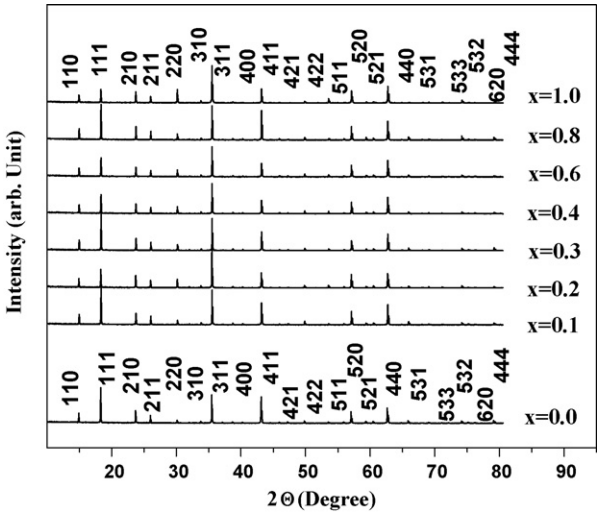

Fig. 2. X-ray diffraction patterns of $Li_2Mg_{1-x}Zn_xTi_3O_8$ ($x = 0$, 0.1, 0.2, 0.3, 0.4, 0.6, 0.8, and 1) ceramics sintered at 1075 °C/4 h.