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Materials Letters 60 (2006) 2814–2818
materials letters
www.elsevier.com/locate/matlet

Effect of ZnO doping on the microwave dielectric properties of $LnTiNbO_6$ (Ln = Sm or Dy) ceramics

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Received 19 December 2005; accepted 31 January 2006
Available online 20 February 2006

Abstract

$LnTiNbO_6$ (Ln = Sm or Dy) ceramics, doped with ZnO, were prepared in the solid-state ceramic route. The cylindrical samples were sintered at temperatures between 1260 and 1385 °C. The densities were measured using Archimedes method. Samples were characterized by X-ray diffraction and scanning electron microscopic methods. Microwave dielectric properties of the cylindrical samples were measured using the network analyzer. Doping of ZnO reduced the sintering temperature and increased the dielectric constant (ε_r). The variation of the resonant frequency with respect to temperature was reduced with the increase in doping concentration. The unloaded quality factor ($Q_u \times f$) is also improved for low doping concentrations. These materials can be used as dielectric resonators in microwave circuits.

Keywords: Ceramics; Sintering; Doping; Dielectric resonators; Microwave dielectrics

1. Introduction

Ceramic materials have high heat resistance and are either insulators or semiconductors with varying magnetic and dielectric properties. In comparison with metallic cavity resonators, ceramic materials are more suitable as dielectric resonators (DRs) in communication systems due to their compactness, thermal stability, low-cost of production, high efficiency and adaptability to microwave integrated circuits [1]. The important characteristics required for DRs are high dielectric constant for miniaturization, low loss for selectivity and low temperature variation of resonant frequency for stability.

Sebastian et al. have reported the microwave dielectric properties of $RETiNbO_6$ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Y and Yb) ceramics [2]. They observed that lower rare earths (atomic numbers 57–63) form ceramics of aeschynite orthorhombic structure having a positive temperature coefficient of resonant frequency (τ_f) with a high dielectric constant while higher rare earths (atomic numbers 64–71) form ceramics of euxenite orthorhombic structure having a negative τ_f with a lower dielectric constant. Recently $RETiNbO_6$ (RE = rare earth metal) is reported as a useful ceramic material, which finds application as dielectric resonator [3,4]. Many other dielectric resonator materials also have been reported which find application in the microwave field [5–11]. The effect of sintering time on the microwave dielectric properties and crystal structure of Y_2BaZnO_5 ceramic was investigated by Akinori Yoshida et al. [12]. Fang et al. have reported $Ba_3La_2Ti_2Nb_2O_{15}$ and $Ba_2La_3Ti_3NbO_{15}$ as ceramics suitable for dielectric resonators [13]. Both of these materials have $A_5B_4O_{15}$ type cation-deficient hexagonal perovskite structure having high dielectric constant and low τ_f value.

The effect of doping on the dielectric properties of cerium oxide as a ceramic dielectric resonator is studied by Santha et al. [14]. Solomon et al. have studied the effect of bismuth oxide addition in the barium rare earth titanate system [15]. The effect of doping with $MnCO_3$ and SnO_2 on $BaO–TiO_2–ZnO$ system was studied by Wang et al. [16]. Huang and Chiang have studied the effect of CuO addition on the microwave dielectric properties and the microstructure of $ZnTa_2O_6$ ceramics [17]. They have showed that zero temperature coefficient of the resonant frequency can be achieved by properly adjusting the concentration of additives.

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doi:10.1016/j.matlet.2006.01.097

In this paper we report the effect of ZnO doping on the sintering and microwave dielectric properties of $LnTiNbO_6$ (Ln = Sm,Dy) ceramics. The microstructure is analysed using scanning electron microscopy (SEM) and the structure is confirmed using X-ray diffraction (XRD) patterns.

2. Experimental

The samples were prepared by the conventional solid-state ceramic route. Analar samples of metal oxides (CDH, 99.9%) were weighed in stoichiometric ratios and mixed thoroughly in acetone medium in an agate mortar. The samples were dried and calcined at 1200 °C for 5 h in electrically heated furnace. A definite mass of calcined powder was mixed with 1 wt.% zinc oxide and ground well. To this 5% polyvinyl alcohol was added as a binder and again ground well and dried. The powder was then pressed in the form of a cylindrical pellet at 100 MPa pressure using a hydraulic press. In a similar way pellets were made with 2, 4 and 6 wt.% doping. Samples were also prepared without doping. The pellets were then sintered as follows. Initially they were heated at a rate of 4 °C/min up to 600 °C and soaked for an hour in order to expel the polyvinyl alcohol. Then, it was heated at a rate of 5 °C/min up to the sintering temperature and soaked for 4 h. The furnace was then cooled slowly to a lower temperature.

The sintered samples were polished well and the densities were measured using Archimedes method. Polished samples were thermally etched at a temperature that is 50 °C below the sintering temperature and used for SEM. Powdered samples were used for X-ray diffraction studies using Cu K_α radiation. The dielectric properties of the samples were measured in the microwave frequency range using the network analyzer. The specimen was placed at the center of a cylindrical cavity whose size is 3–4 times greater than it. The microwave was coupled to the specimen through E-field probes and $TE_{01\delta}$ mode of resonance whose quality factor is intimately related to the dielectric loss, was identified. The dielectric constant (ε_r) and the unloaded quality factor ($Q_u \times f$) were then calculated using the computer interfaced network analyzer. The coefficient of thermal variation of resonant frequency (τ_f) was also measured over a range of temperature 20–80 °C.

3. Results and discussion

The microwave dielectric properties of Zinc oxide doped samples of $SmTiNbO_6$ and $DyTiNbO_6$ are given in Tables 1 and 2, respectively. The sintering temperature of the doped sample decreases with the increase in doping concentration.

Table 1
Microwave dielectric properties of ZnO-doped $SmTiNbO_6$ ceramics

Percentage of ZnO	Frequency (GHz)	$Q_u \times f$ (GHz)	Dielectric constant (ε_r)	τ_f (ppm/K)	Sintering temperature (°C)
0	4.8900	7640.0	44.05	50	1360
1	4.5444	10367.9	46.39	49	1360
2	4.3663	14190.2	47.90	48	1340
4	4.4916	8950.0	44.57	40	1310
6	4.6628	3749.7	41.09	31	1260

Table 2
Microwave dielectric properties of ZnO-doped $DyTiNbO_6$ ceramics

Percentage of ZnO	Frequency (GHz)	$Q_u \times f$ (GHz)	Dielectric constant (ε_r)	τ_f (ppm/K)	Sintering temperature (°C)
0	7.7600	19100	21.01	−42	1385
1	5.5696	19200	21.37	−32	1370
2	5.5003	14368	21.84	−29	1370
4	5.5264	8898	21.58	−24	1340
6	5.5624	4070	20.56	−20	1340

Fig. 1 shows that the dielectric constant and the density of $SmTiNbO_6$ ceramics increase with the increase in the percentage of doping of ZnO initially, reach a maximum value, and then decrease. The $Q_u \times f$ value also shows a similar variation as shown in Fig. 2. This is due to the formation of secondary phases in the highly doped (>2%) samples as reported earlier [18–21]. Fig. 3 shows that the τ_f decreases with the increase in the percentage of doping of ZnO and obtaining greater thermal stability. The 1% and 2% ZnO-doped sample with relatively high ε_r, high $Q_u \times f$ and low τ_f is a suitable material to use as a DR.

Fig. 4 shows that the dielectric constant and the density of $DyTiNbO_6$ ceramics increase with the increase in the percentage of

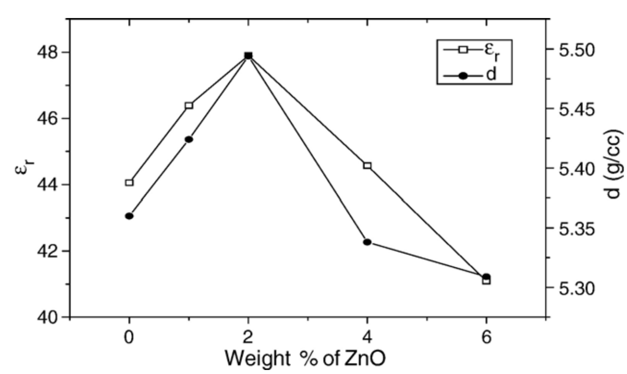

Fig. 1. Variation of dielectric constant (ε_r) and density (d) of $SmTiNbO_6$ with the wt.% of ZnO doped.

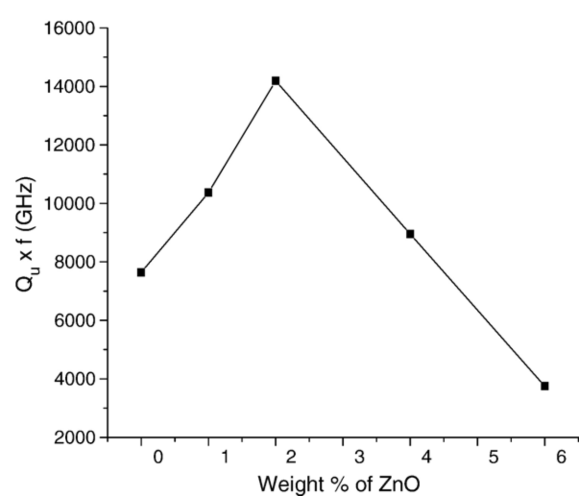

Fig. 2. Variation of $Q_u \times f$ of $SmTiNbO_6$ with the wt.% of ZnO doped.