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Preparation, Characterization, and Microwave Properties of $RETiNbO_6$ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, and Yb) Dielectric Ceramics

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Microwave ceramic dielectric resonators (DRs) based on RE-$TiNbO_6$ (RE = Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Y, and Yb) have been prepared using the conventional solid-state ceramic route. The DR samples are characterized using XRD and SEM methods. The microwave dielectric properties are measured using resonant methods and a net work analyzer. The ceramics based on Ce, Pr, Nd, and Sm have dielectric constants in the range 32–54 and positive coefficient of thermal variation of resonant frequency (τ_f). The ceramics based on Gd, Tb, Dy, Y, and Yb have dielectric constants in the range 19–22 and negative τ_f.

I. Introduction

Ceramic materials with temperature-stable high dielectric constant and low loss are used as microwave dielectric resonators (DRs) in modern communication systems. The advantages that ceramics have over other materials are compactness, thermal stability, low cost of production, high efficiency, and adaptability to microwave integrated circuits (MICs). The important characteristics required for a DR are high dielectric constant for miniaturization, low loss for selectivity, and low temperature variation of the resonant frequency for stability. Several DR materials, such as $Ba_2Ti_9O_{20}$, $(Zr,Sn)TiO_4$, $Ba(RE_{1/2}Nb_{1/2})O_3$, $Ba(Mg_{1/3}Ta_{2/3})O_3$, and $BaO–Nd_2O_3–TiO_2$, have been investigated[1–12] for microwave applications. The search for new ceramic dielectric materials continues. In the present paper, we report the microwave dielectric properties of $RETiNbO_6$ (RE = rare earth) ceramics. The RE-$TiNbO_6$ compounds are reported[13–18] as orthorhombic with space group *Pnma*, $Z = 4$, and isostructral with minerals of the aeschnite–priorite group. The compounds with RE atomic number 64–71 (RE = Gd, Tb, Er, Yb) show an additional high-temperature isostructural form with euxenite–polycrase group, having space group *Pcan*.[13–15]

II. Experimental Procedure

The $RETiNbO_6$ ceramics were prepared using the conventional solid-state ceramic route. The starting materials were the oxides of the respective elements (i.e., RE_2O_3, Nb_2O_5, and TiO_2) and were wet mixed in distilled water. After it was mixed and ground, the slurry was dried, ground again for 2 h, and calcined at 1250°C for 4 h. The calcined powder was ground well for 2 h, and 5% poly(vinyl alcohol) (PVA) was added as binder. The slurry was mixed well and dried and ground again for 2 h. The fine powder thus obtained was used to prepare cylindrical compacts of 10 mm diameter and 5–7 mm thickness, using a tungsten carbide (WC) die under a pressure ~175 MPa. These pellets were fired at a rate of 5°C/min up to 600°C and then 10°C/min up to the sintering temperature. An intermediate soaking was performed at 600°C for 1 h to expel the binder. The sintering temperature was optimized by sintering the samples at various temperatures. The bulk density was measured after sintering at each temperature and a graph was drawn of the temperature versus the bulk density. The temperature above which the graph showed almost zero slope was taken as the sintering temperature. The sintering temperatures of the compounds were in the range 1360°–1400°C for 4 h in air (see Table I). After the sintering was complete, the furnace was allowed naturally cool by turning off the electric power.

The sintered samples were powdered and used for recording X-ray diffraction (XRD) patterns using Cu*K* radiation. The sintered ceramics were well polished, thermally etched for 30 min at 1325°C, and the surfaces observed using scanning electron microscopy. The microwave dielectric properties were measured using a net work analyzer (Model HP 8510C, Hewlett–Packard, Palo Alto, CA). The dielectric constant was determined using the end-shorted method of Hakki and Coleman.[19] The quality factors of the samples were measured using the stripline method of Khanna and Garault.[20] The TE_{011} mode was used for all measurements.

III. Results and Discussion

The powder XRD patterns of $RETiNbO_6$ ceramics are given in Figs. 1 and 2. The powder patterns are indexed, and the lattice parameters are calculated and are given in Table I. Except for $EuTiNbO_6$, all XRD patterns are in agreement with ICDD files.[21] The Ce-, Pr-, Nd-, and Sm-based ceramics have similar XRD patterns and have orthorhombic $CaTa_2O_6$ structure with space group *Pnma* (*D*2*h*16).[18,22,23] Similarly, the XRD patterns of Gd-, Tb-, Dy-, and Y-based ceramics are similar, and they have an orthorhombic columbite structure with space group *Pbcn* (*D*2*h*14) as reported earlier.[18,24,25] The XRD pattern of $EuTiNbO_6$ is different from euxenite and aeschnite structures, and a detailed analysis is needed to confirm the structure and symmetry of this compound. The theoretical and the experimental density decreases and cell volume increases with crystal radii of $RETiNbO_6$ compounds.

The dielectric constants of $RETiNbO_6$ samples are given in Table II, which shows that the dielectric constant decreases from $CeTiNbO_6$ to $EuTiNbO_6$, depending on ionic radii of the rare-earth ion in the aeschnite group. Of all the five compounds of the aeschnite group, Eu has a low dielectric constant compared to other materials. However, there is no considerable variation in the dielectric constant values for the materials in the euxenite group, i.e., from Gd to Y. All the compounds have relatively high quality factors (see Table II). The quality factors reported here are equal to those that can be obtained in an actual working environment, because the measurement has been done using the stripline

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Table I. Density and Lattice Parameters of $RETiNbO_6$ Ceramics

Rare earth	Density (g/cm^3) Experimental	Density (g/cm^3) Theoretical	Percent of theoretical density	Lattice parameter (Å) *a*	Lattice parameter (Å) *b*	Lattice parameter (Å) *c*	*c/a*
Ce	5.3	5.56	95	11.03	7.58	5.42	0.491
Pr	5.4	5.67	96	11.01	7.45	5.39	0.489
Nd	5.5	5.82	94	10.95	7.47	5.34	0.487
Sm	5.6	5.92	96	11.01	7.47	5.31	0.483
Eu	5.6			10.94	7.41	5.25	0.479
Gd	5.8	6.26	93	14.63	5.16	5.57	0.381
Tb	5.9	6.3	94	14.56	5.19	5.56	0.382
Dy	6.1	6.42	95	14.53	5.17	5.53	0.381
Y	4.8	5.26	92	14.88	5.03	5.52	0.371
Yb	6.4	6.8	94	15.34	5.13	5.13	0.334

Table II. Microwave Dielectric Properties of $RETiNbO_6$ Ceramics

Rare earth	Dielectric constant	$TE_{01\delta}$ (GHz)	Quality factor (10^3 GHz)	τ_f (ppm/K)	Rare-earth crystal radii (Å)	Sintering temperature (°C)
Ce	54	4.44	6.53	67	1.174	1,360
Pr	53	4.85	12.3	56	1.153	1,370
Nd	52	4.93	4.48	46	1.135	1,370
Sm	45	6.4	18.0	50	1.104	1,360
Eu	32	5.3	17.25	5	1.09	1,370
Gd	20	7.27	9.06	−52	1.078	1,385
Tb	21	7.58	15.7	−45	1.063	1,385
Dy	22	7.76	19.1	−42	1.048	1,385
Y	19	8.18	8.82	−45	1.032	1,400
Yb	22	7.4	11.0	−63	0.998	1,400

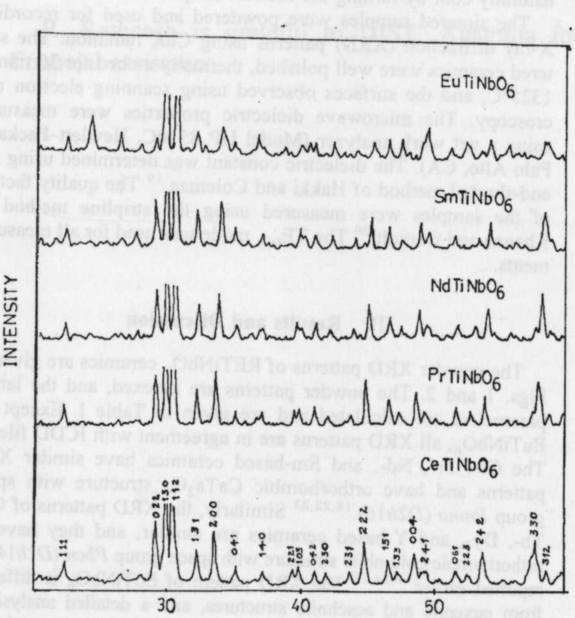

Fig. 1. XRD pattern recorded for $RETiNbO_6$ (RE = Ce, Pr, Nd, Sm, and Eu) using Cu*K* radiation.

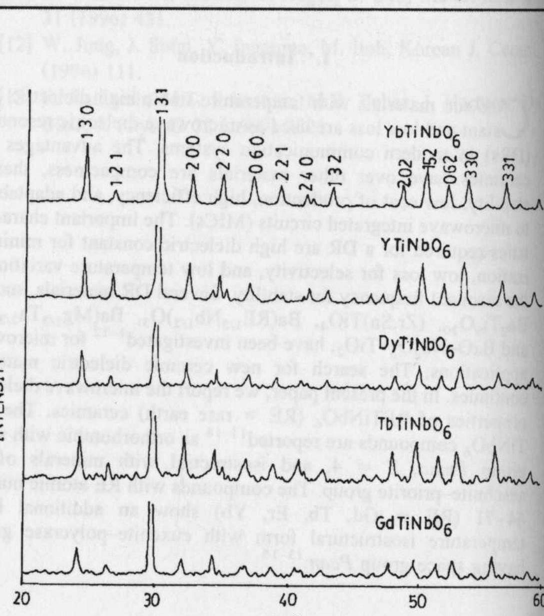

Fig. 2. XRD pattern recorded for $RETiNbO_6$ (RE = Gd, Tb, Dy, Y, and Yb) using Cu*K* radiation.

method. In ceramics, the extent of porosity, grain size, dislocations, and lattice defects vary from sample to sample. These factors have profound influence on the quality factor of these materials. Hence, the various samples prepared for a particular compound may have slightly different quality factors. However, the inherent quality factor of these materials is higher than what is reported here. The stripline method for the quality factor measurements involves additional losses because of resonator shape applications, radiation losses, conductor losses, etc. Nevertheless, the obtained dielectric losses (tan δ) of these compounds are expected to be in the range of 10^{-3} in the C-band (4–8 GHz).

IV. Conclusion

$RETiNbO_6$ ceramics have been prepared as a new DR material by the conventional solid-state ceramic route and characterized using XRD, SEM, and microwave methods. The structure and dielectric properties depend on the ionic radii of the rare-earth ion. The ceramics with RE = Ce, Pr, Nd, and Sm show dielectric constants in the range 46–54. These high-dielectric-constant materials show positive coefficient of thermal variation of resonant frequency (τ_f). The ceramics with RE = Gd, Tb, Dy, Y, and Yb have negative τ_f and dielectric constant in the range 19–22. The unloaded quality factors of the ceramics are >1500 at ~3 GHz. The Eu compound has a dielectric constant and τ_f between those of aeschnite and euxenite compounds. $EuTiNbO_6$ has a high quality factor and low temperature variation of resonant frequency and is a possible material for microwave resonator applications. These materials are also useful for capacitative applications or random acess memory (DRAM) devices.[26] Preliminary studies show that it is possible to lower the τ_f by preparing a solid-solution phase between the euxenite and the aeschnite compounds, and the results will be reported later.

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