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Materials Chemistry and Physics 67 (2001) 291–293

MATERIALS CHEMISTRY AND PHYSICS

www.elsevier.com/locate/matchemphys

Synthesis, characterization and properties of $[RE_{1-x}RE'_x]TiNbO_6$ dielectric ceramics

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Abstract

Dielectric ceramics based on solid solution phases of $[RE_{1-x}RE'_x]TiNbO_6$, where RE_{1-x} = Nd, Pr, Sm and RE'_x = Dy, Gd and Y, were prepared by the conventional solid-state ceramic route for values of x. The ceramic samples are characterized by X-ray diffraction and microwave methods. Ceramics based on RE (Pr, Nd and Sm) belonging to aeschynite group shows positive value of τ_f and those based on RE (Gd, Dy and Y) belonging to euxenite group show negative value of τ_f. The solid solution phases between the aeschynite and the euxenite group shows intermediate dielectric constant and τ_f values. The results indicate the possibility of tailoring the dielectric properties by varying the composition of the solid solution phases. The range of solid solubility of euxenite in aeschenite and aeschenite in euxenite are different for different rare earth ions.

Keywords: Dielectric resonators; Ceramic resonators; Dielectric ceramics; Rare earth titanium niobate; Microwave ceramics

1. Introduction

With the recent advances in microwave telecommunication and satellite broadcasting, a variety of microwave devices have been developed using dielectric resonators as the frequency determining components. Dielectric resonators (DRs) provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the production of high frequency devices. The important characteristics required for a DR are high dielectric constant for miniaturization, high quality factor for selectivity and low temperature variation of resonant frequency for stability. Several DR materials have been investigated [1–9] for microwave applications. Still the search for new materials having these properties is in progress. Recently $RETiNbO_6$ (RE: rare earth ion) is reported as a useful ceramic material for dielectric resonator applications [10–12]. Single crystals of these groups of materials are recently reported as useful for miniature solid state and diode pumped lasers [13,14] because of their interesting optical properties. In 1963, Komkov [15] synthesized $RETiNbO_6$ compounds by hydrothermal synthesis from equivalent mixtures of RE_2O_3, TiO_2 and Nb_2O_5.

The $RETiNbO_6$ compounds with atomic number of the rare earth ion in the range of 57–63 are known [13–15] to crystallize with orthorhombic aeschynite crystal structure with four formula units per unit cell and space group Pnma. Compounds with atomic number of the rare earth ion in the range of 64–71 have euxenite structure. The euxenite structure is also orthorhombic but of a different symmetry with space group Pcan. The members of aeschynite group are known [10–12] to have positive τ_f with high ε and that of euxenite group have negative τ_f with relatively low ε (see Table 1). Hence by preparing the solid solution phases between positive and negative τ_f materials it may be possible to tailor microwave dielectric properties. This paper discuss the synthesis characterization and microwave dielectric properties of solid solution phases in $[RE_{1-x}RE'_x]TiNbO_6$.

2. Experimental

The $[RE_{1-x}RE'_x]TiNbO_6$, where RE_{1-x} = Nd, Pr, Sm and RE'_x = Dy, Gd and Y, were prepared by the conventional solid-state ceramic route. The oxides of the rare earths, titanium and niobium were weighed in the appropriate molar ratio and thoroughly mixed in an agate mortar using acetone as mixing medium. The powder was dried and calcined at 1260°C for 4 h in air. The calcined powder was again ground well and 5% polyvinyl alcohol was added as binder and the mixture was again ground before being pressed to cylinders of 10 mm diameter and 7–8 mm length at about 150 MPa pressure. The pellets were sintered at 1360–1400°C

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0254-0584/01/$ – see front matter
PII: S0254-0584(00)00453-3

Table 1
Properties of $RETiNbO_6$ ceramics (after Ref. [7–9])

RE, ionic radius (Å)	Density ($g\,cm^{-3}$)	ε_r	τ_f (ppm per °C)	$Q \times F$ (GHz)	Cell volume ($Å^3$)
Pr (1.153)	5.67	53	56	12300	442.1
Nd (1.135)	5.48	52	46	4480	437.3
Sm (1.104)	5.36	44	50	7640	436.7
Gd (1.078)	5.75	20	−52	9060	420.3
Dy (1.048)	6.01	21	−42	19100	415.7
Y (1.032)	4.60	19	−45	8820	413.2

for 4 h in air on platinum plates. The sintered pellets were polished and used for making physical property measurements. The bulk densities of the pellets were measured using Archimedes method. Powdered samples were used for X-ray powder diffraction analysis using CuKα radiation.

3. Microwave characterization

The microwave characterization of the samples was done using a network analyzer (HP 8510 C). The dielectric constant was measured by Hakki and Coleman method [16] with the dielectric placed in between two conducting plates. The Q factor was measured by the microstripline method of Khanna and Garault [17]. The coefficient of thermal variation of resonant frequency (τ_f) was measured by noting the temperature variation of resonant frequency of TE_{011} mode over the range of temperature 25–80°C.

4. Results and discussion

Table 2 shows the microwave dielectric properties of $Pr_{1-x}Gd_xTiNbO_6$ samples. The substitution of Gd at the Pr site decreases the dielectric constant and the τ_f value as a function of x. The solid solution phases have the symmetry and structure of the aeschynite group for $x > 0.2$. The $GdTiNbO_6$ dissolves in $PrTiNbO_6$ up to 80 mol% to form $Pr_{1-x}Gd_xTiNbO_6$. For $x < 0.2$, the structure changes to that of the euxenite group. The τ_f values of solid solution phases for $x < 0.2$ have negative values. Further work is needed to know the exact value of x at which the aeschenite to euxenite transition occurs and to obtain a zero τ_f material. Table 3 shows the dielectric properties of $Sm_{1-x}Y_xTiNbO_6$

Table 2
The microwave dielectric properties of $Pr_{1-x}Gd_xTiNbO_6$

x	ε	$Q \times F$ (GHz)	τ_f (ppm per °C)	Sintering temperature (°C)
1.0	53	12400	56	1370
0.8	49	9500	54	1400
0.5	46	9500	41	1400
0.2	41	4500	37	1400
0.1	25	3375	−15	1385
0.0	20	9000	−52	1385

Table 3
Microwave dielectric properties of $Sm_{1-x}Y_xTiNbO_6$

x	ε	$Q \times F$ (GHz)	τ_f (ppm per °C)	Sintering temperature (°C)
1.0	44	7640	50	1360
0.8	30	11000	17	1400
0.7	22	13300	−2	1400
0.6	21	11500	−4	1400
0.5	21	15500	−21	1420
0.2	20	13800	−29	1420
0.0	19	8800	−45	1400

Table 4
Microwave dielectric properties of $Nd_{1-x}Dy_xTiNbO_6$

x	ε	$Q \times F$ (GHz)	τ_f (ppm per °C)	Sintering temperature (°C)
1	52	5000	46	1380
0.9	48	3000	40	1380
0.7	43	17000	30	1380
0.5	31	28000	−13	1385
0.3	24	13000	−20	1385
0.1	22	28500	−32	1385
0	21	19000	−42	1380

ceramics. The $YTiNbO_6$ forms solid solution phases in $SmTiNbO_6$ for $x > 0.8$ with the structure and symmetry of the aeschynite group. For $x < 0.8$, it forms solid solution phases with the structure and symmetry of the euxenite group and have negative τ_f. The dielectric constants of the phases in the euxenite group are relatively low as compared to those in the aeschynite group. In $Nd_{1-x}Dy_xTiNbO_6$, the solid solution phases have the aeschynite structure up to $x > 0.7$ with a high dielectric constant and positive τ_f (Table 4). For $x < 0.5$, they are euxenite with negative τ_f.

5. Conclusions

Solid solution phases of $[RE_{1-x}RE'_x]TiNbO_6$, where RE_{1-x} = Nd, Pr, Sm and RE'_x = Dy, Gd, Y, respectively, were synthesized for different values of x by the conventional solid-state ceramics route and were characterized by microwave methods. The dielectric properties vary linearly as a function of x until a phase transition (aeschenite–euxenite) occurs. Again the dielectric properties vary linearly as a function of x in the new phase. The range of solid solubility of aeschynite in euxenite and euxenite in aeschynite depend on the rare earth ions. The τ_f of the materials are improved by the solid solution formation. Further work is in progress to understand the mechanism of phase transition, dielectric properties of the ceramics near the transition point, to find the exact values of x at which the transition occur and to know whether it is possible to get zero τ_f materials.

Acknowledgements

The authors are thankful to Dr. U. Shyamaprasad and Mr. P. Guruswamy for their kind help in XRD analysis. The authors are grateful to Defense Research and Development Organization (DRDO), New Delhi for financial support to carry out the research work.

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