

**SAMARIUM TITANIUM NIOBATE (SmTiNbO_6):
A NEW MICROWAVE DIELECTRIC CERAMIC**

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ABSTRACT

SmTiNbO_6 ceramics have been prepared by conventional solid state ceramic routes. The sintered ceramic samples were characterized by X-ray diffraction and SEM methods. The dielectric properties of the samples were measured in the microwave frequency region. The material has a high dielectric constant ($\epsilon_r \sim 45$), high unloaded quality factor (2900 at 6.42 GHz), and small temperature variation of resonant frequency ($\tau_f \sim +50$ ppm/K), and is a possible material for applications such as dielectric resonators in microwave circuits. © 1997 Elsevier Science Ltd

KEYWORDS: A. electronic materials, A. oxides, D. dielectric properties

INTRODUCTION

Recent progress in microwave integrated systems for telecommunication and satellite television demands the development of a variety of hyperfrequency devices for filters and frequency-stabilized oscillators. Dielectric resonators provide significant advantages in terms of compactness, light weight, temperature stability, and relatively low cost of production of microwave devices. The important characteristics of a dielectric resonator are (i) high dielectric constant ' ϵ_r ' (>20) in order to miniaturize the size of the resonators, (ii) high Q factor ($>1,000$) at operating frequencies to minimize band width, and (iii) a small temperature coefficient of resonant frequency ($\tau_f < \pm 25$ ppm/K), which is important for stability. In 1960, Okaya (1) reported rutile (TiO_2) as the first dielectric resonator material with a high Q value ($Q \sim 10,000$ at 4 GHz) and $\epsilon_r \sim 104$. However, the temperature

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coefficient of resonant frequency $\tau_f \sim +427$ ppm/K was too large to be used in practical applications. Recently, ceramic compounds with relative permittivities (ϵ_r) in the range 20 to 100, such as complex perovskites (2–5), the ZrO_2 – SnO_2 – TiO_2 system (6–8), $Ba_2Ti_9O_{20}$ (9–11), the BaO – Ln_2O_3 – TiO_2 ($Ln = La, Nd, Sm, Pr$) system (12–17), and $Ba_5Nb_4O_{15}$ (18), have been investigated for practical applications. BaO – Ln_2O_3 – TiO_2 compounds with high permittivities ($\epsilon_r = 70$ –100) are used in the 800 MHz mobile telephone system to miniaturize circuit dimensions, and $Ba_2Ti_9O_{20}$ is presently used extensively in all base stations.

In the present paper, we report a new microwave dielectric resonator material. Komkov (19) prepared $SmTiNbO_6$ hydrothermally at 250–300°C from equivalent mixtures of Sm_2O_3 , Nb_2O_5 , and $2TiO_2$. They belong to the $Pbnm$ (D_{2h}^{16}) space group with $z = 4$. The samples prepared by heat treatment at 1300°C gave the same structure (19). $SmTiNbO_6$ is isostructural with minerals of the aeschynite-priorite group. The preparation characterization and dielectric properties of $SmTiNbO_6$ dielectric ceramic are described in this paper.

CERAMIC PREPARATION AND CHARACTERIZATION

The samples were prepared by the solid-state ceramic route. Stoichiometric amounts of high-purity TiO_2 , Nb_2O_5 , and Sm_2O_3 were weighed and wet-mixed using acetone for about 1 hour, dried, and then calcined at 1270°C for 4 hours in a platinum crucible. The sample was then ground again for 1 hour and the fine powder thus obtained was pressed (120 MPa) into cylindrical discs about 10 mm in diameter and 6–9 mm thick. The pellets were sintered at 1360°C for 4 hours. The sintered pellets were colorless and had a relative density of 90% (Archimedes method). The sintered ceramic samples were characterized using X-ray diffraction (XRD) and scanning electron microscopy (SEM) methods. The dielectric constant and unloaded quality factor at microwave frequencies were measured using a Hewlett Packard 8510B Network Analyzer and a Hewlett Packard 8514 B Reflection-Transmission unit. The apparatus was controlled using a Hewlett Packard 9000, 300 series computer. The ϵ_r was calculated from the TE_{011} resonance mode of the end-shortened sample placed between two conducting plates, using the method of Hakki and Coleman (20) and modified by Courtney (21). The Q factor was measured by the microstripline method of Khanna and Garault (22) and is the Q that can be achieved in an actual working

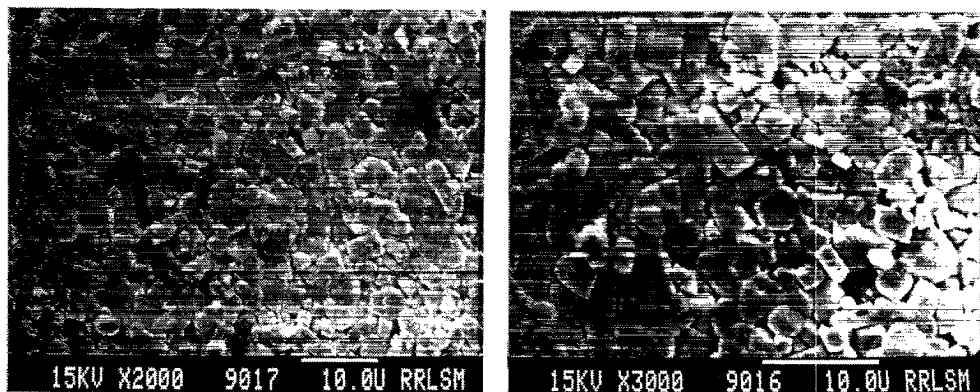


FIG. 1
SEM photographs of $SmTiNbO_6$.

environment. The coefficient of temperature variation of resonant frequency was measured by noting the temperature variation of resonant frequency of the TE₀₁₁ mode in the transmission configuration over a range of temperature 23–80°C.

RESULTS AND DISCUSSION

The XRD pattern recorded from a sintered and powdered SmTiNbO₆ sample is in agreement with JCPDS file card no. 20-1470. The SmTiNbO₆ is orthorhombic with $a = 5.31$, $b = 11.01$, and $c = 7.47$ Å. Figure 1 shows the microstructure of a typical sample taken after thermal etching. The SEM pictures show uniform distribution of grains approximately 3 μm in size, with single phase nature. Figure 2 shows the TE₀₁₁ resonance at 4.898 GHz of a typical sample, which is 9.96 mm in diameter and 8.26 mm in length. The dielectric constant of the sample with 90% density is 45. The dielectric constant is calculated theoretically using the Clausius-Mossotti equation (23,24)

$$\epsilon = \frac{3V_m + 8\pi\alpha}{3V_m - 4\pi\alpha}$$

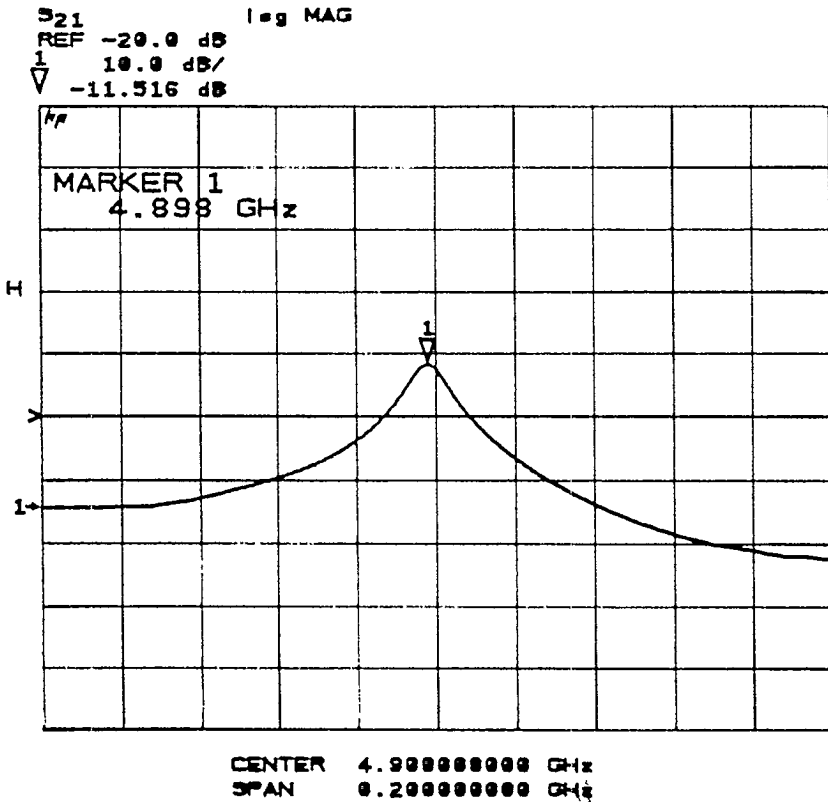


FIG. 2
TE₀₁₁ resonant mode of a typical SmTiNbO₆ resonator.

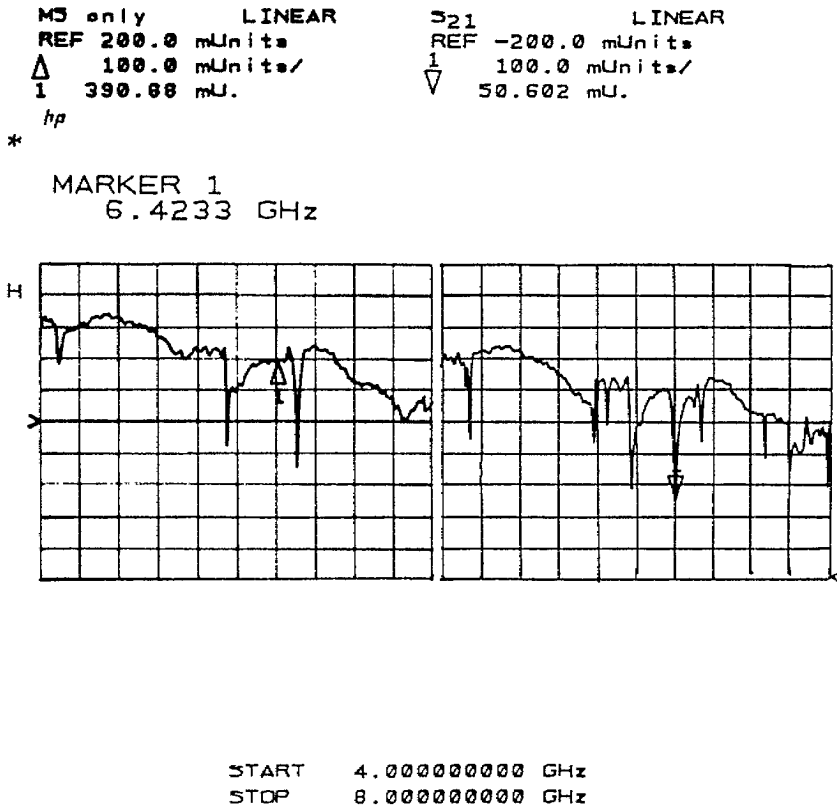


FIG. 3

Resonant modes of SmTiNbO_6 ceramic when coupled to a microstripline enclosed in a brass cavity and the modes of cavity alone.

where V_m is the molar volume and α is the total molar dielectric polarizability of the compound and can be calculated as a simple linear combination of individual ion dielectric polarizabilities given by Shannon (24). The $\epsilon_{\text{calc.}}$ is 31 and is different from the observed value 45. The difference is attributed to inaccuracies in the polarizabilities, deviations from cubic structure, and the fact that the studied material is a ceramic and not a single crystal. The polarizability, α , equals the sum of the polarizabilities of all atoms in a unit cell with volume, V , only if all the atoms in the structure have a cubic environment (23). The band rejection filter using the dielectric resonator, coupled to the stripline and enclosed in a brass enclosure of $5 \times 5 \times 3 \text{ cm}^3$, showed a sharp and well-separated cut-off with transmission coefficient of 0.032 units at 6.42 GHz. Figure 3 shows the variation of the transmission coefficient of SmTiNbO_6 when coupled to a microstripline. The width of the resonant curve (Δf) corresponding to the transmission coefficient calculated using the formula (21)

$$S_{21U} = S_{21} \sqrt{\frac{2}{1 + S_{21}^2}}$$

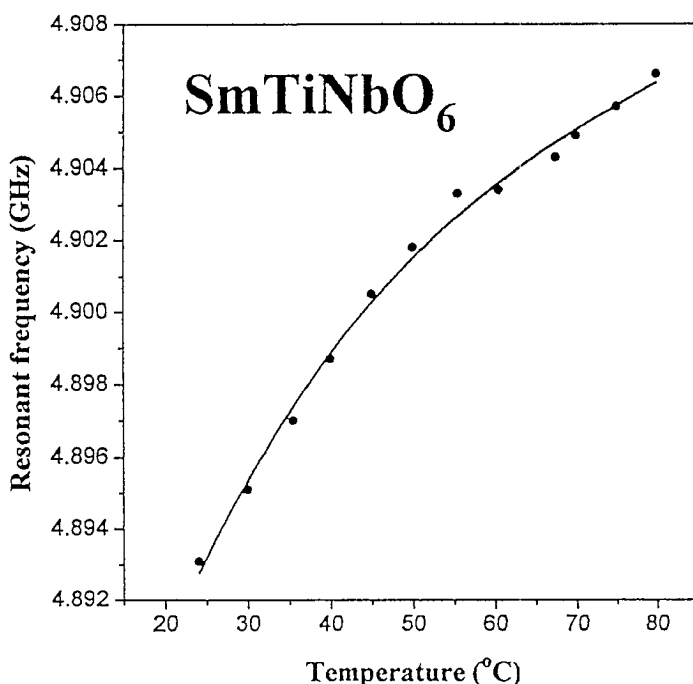


FIG. 4

Variation of resonant frequency with temperature of SmTiNbO₆ ceramics.

was 2.173 MHz, giving a Q value of 2952. Calibration for full transmission was done without DR. The thermal variation of resonant frequency is shown in Figure 4. The resonant frequency increases with increase in temperature. The temperature coefficient of resonant frequency of SmTiNbO₆ is +50 ppm/K.

CONCLUSION

SmTiNbO₆ ceramics have been prepared and characterized using XRD and SEM. The dielectric properties were measured in microwave frequency regions. A ceramic sample with 90% theoretical density exhibited a dielectric constant of 45, unloaded quality factor above 2900 at 6.42 GHz, and a coefficient of temperature variation of resonant frequency 50 ppm/K. The SmTiNbO₆ is a possible dielectric resonator ceramic for microwave applications. It is possible to replace Sm by other rare-earth elements such as La, Pr, and Nd, and such work is in progress with a view of finding new materials.

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REFERENCES

1. A. Okaya, *Proc. Inst. Radio Engineers* **48**, 1921 (1960).
2. H. Tamura, T. Konoike, Y. Sakabe and K. Wakino, *J. Am. Ceram. Soc.* **67**, C-59 (1984).
3. M. Takata and K. Kageyama, *J. Am. Ceram. Soc.* **72**, 1955 (1989).
4. H. Sreemoolanadhan, J. Isaac, M.T. Sebastian, K.A. Jose and P. Mohanan, *Ceram. Int.* **21**, 385 (1995).
5. S. Nomura, K. Toyama and K. Kaneta, *Jpn. J. Appl. Phys.* **21**, L624 (1982).
6. K. Wakino, K. Minai and H. Tamura, *J. Am. Ceram. Soc.* **67**, 278 (1984).
7. G. Wolfram and H.E. Gobel, *Mater. Res. Bull.* **16**, 1455 (1981).
8. H. Hirano, T. Hayashi and A. Hattori, *J. Am. Ceram. Soc.* **74**, 1320 (1991).
9. H.M. O'Bryan, J. Thomson and J.K. Plourde, *J. Amer. Ceram. Soc.* **57**, 450 (1974).
10. J.K. Plourde, D.F. Linn, H.M. O'Bryan and J. Thomson, *J. Am. Ceram. Soc.* **58**, 418 (1975).
11. H. Sreemoolanadhan, J. Isaac, P. Koshy, M.T. Sebastian, K.A. Jose and P. Mohanan, *Br. Ceram. Trans. J.* **94**, 157 (1995).
12. D. Kolar, S. Gaberscek, Z. Stadler and D. Suvorov, *Ferroelectrics* **27**, 267 (1980).
13. J.P. Mercurio, M. Manier and B. Frit, *Mater. Lett.* **8**, 112 (1989).
14. P. Laffez, G. Desgardin and B. Raveau, *J. Mater. Sci.* **27**, 5229 (1990).
15. J. Wu and M. Chang, *J. Am. Ceram. Soc.* **73**, 1599 (1990).
16. X.M. Chen, Y. Suzuki and N. Sato, *Mater. Lett.* **16**, 75 (1993).
17. H. Sreemoolanadhan, M.T. Sebastian and P. Mohanan, *Br. Ceram. Trans. J.* **95**(2), 79 (1996).
18. H. Sreemoolanadhan, M.T. Sebastian and P. Mohanan, *Mater. Res. Bull.* **30**, 653 (1995).
19. A.I. Komkov, *Dokl. Akad. Nauk. SSSR* **148**, 1182 (1963).
20. B.W. Hakki and P.D. Coleman, *IRE Trans. Microwave Theory Tech.* **MTT-8**, 402 (1960).
21. W.E. Courtney, *IEEE Trans. Microwave Theory Tech.* **MTT-18**, 476 (1970).
22. A.P.S. Khanna and Y. Garault, *IEEE Trans. Microwave Theory Tech.* **MTT-31**, 262 (1983).
23. R.D. Shannon and M.A. Subramaniam, *Phys. Chem. Minerals* **16**, 747 (1989).
24. R.D. Shannon, *J. Appl. Phys.* **73**, 348 (1993).