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A new group of microwave dielectric ceramics in the RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] system

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RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] ceramics have been prepared as single-phase materials by a conventional solid-state ceramic route. The ceramics have been characterized by X-ray diffraction and microwave methods. The RE($Ti_{0.5}W_{0.5}$)O_4 ceramics showed an increase in cell volume and a corresponding decrease in density with ionic radius of RE^{3+} ions. The dielectric constant varies from 21 to 25, $Q_u \times f$ from 6000 to 11 000 GHz and τ_f from -5 to -22 ppm °C^{-1}. The microwave dielectric properties indicate that these materials are possible candidates for dielectric resonator as well as substrate applications in microwave integrated circuits.

1. Introduction

The rapid development in the microwave electronic industry demands new ceramic components for application in practical circuits. In the modern telecommunication scenario system designers are mainly focusing on the miniaturization of the circuits. This has increased the interest in the development of new high dielectric constant (ε_r) ceramic materials that can be used as resonators in practical circuits, which can reduce the size of the cavity by $\varepsilon_r^{1/2}$ [1]. The important characteristics required for a dielectric resonator (DR) are high dielectric constant for size reduction, high quality factor (Q_u) (low dielectric loss) for selectivity and low temperature coefficient of resonant frequency (τ_f) for frequency stability and better performance in practical circuits. These find widespread applications in different microwave circuits [2–5] like filters, oscillators, and dielectric resonator antennas. Moreover, the versatility and adaptability of DRs have made them indispensable components in modern telecommunication systems, global positioning systems (GPS), mobile phones, radar detectors, substrates for microwave integrated circuits (MIC), and as gate dielectrics. Several (DR) materials [6–9] with varying dielectric properties have been reported by various research groups. But owing to the difficulty in controlling the dielectric properties at microwave frequencies, intense work is continuing in search of new materials with improved properties. Dielectric ceramics, having low or medium ε_r high Q_u low τ_f and good lattice matching with the superconducting material, can be better used as a substrate [10, 11]. In the present paper, we report the microwave dielectric properties of RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] ceramics.

2. Experimental

The RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] ceramics have been synthesized by the conventional solid-state ceramic route. The oxides Pr_6O_{11}, Nd_2O_3, Sm_2O_3, Gd_2O_3, Tb_2O_3, Dy_2O_3, Y_2O_3, TiO_2, and WO_3 with 99.9% purity were used. The stoichoimetric mixtures of the oxides were ball milled using zirconia balls in distilled water medium for 24 h and dried. The powder was then calcined in the range 900–1160 °C for 4 h in air (see Table I). The calcined powders were well ground in an agate and mixed with 4 wt % polyvinyl alcohol (PVA) as the binder and dried again. They were then well ground to form fine powder and shaped into cylindrical compacts of about 14 mm diameter and 7 mm height under a pressure of about 200 MPa. We optimized the sintering temperature of different rare earth titanium tungstates by sintering them at various temperatures [1025–1425 °C for 4 h (see Table I)]. Attempts were made to prepare RE($Ti_{0.5}W_{0.5}$)O_4 with RE = La, Ce, In, and Al. They did not form a single-phase compound.

The bulk densities of the samples were measured by the Archimedes method. The phase purity and structure were studied by X-ray diffraction (XRD) using CuK_α radiation. Well-polished samples were used for microwave dielectric measurements. The dielectric properties such as dielectric constant and unloaded quality factor were measured by using an HP 8510 C network analyzer attached to a sweep oscillator and test unit. The ε_r was

TABLE I Lattice parameters, densities and microwave dielectric properties of RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] and Ce-, La-, In- and Al-based multiphase ceramics

RE	a (nm)	c (nm)	Cell volume (nm^3)	Experimental density (g cm^{-3})	Percentage density	Calcination temperature (°C) (4 h)	Sintering temperature (°C) (4 h)	Experimental $\varepsilon_r(\varepsilon_{re})$	Porosity corrected $\varepsilon_r(\varepsilon_{rc})$	$Q_u \times f$ (GHz)	τ_f (ppm °C^{-1})
Pr	0.525	1.145	0.31445	6.432	94.95	1160	1300	20.23	21.86	6900	− 20
Nd	0.523	1.136	0.30761	6.590	94.28	1150	1285	21.34	23.22	10 600	− 22
Sm	0.520	1.122	0.30128	6.840	93.96	1160	1300	21.51	23.52	7100	− 14
Gd	0.517	1.110	0.29634	6.970	92.32	1160	1375	22.18	24.89	5000	− 10
Tb	0.515	1.108	0.29309	7.086	92.39	1150	1375	19.05	21.33	5900	− 6
Dy	0.512	1.106	0.28869	7.373	93.68	1160	1425	19.85	21.79	6000	− 5
Y	0.511, $b = 0.507$	1.094	0.28398	5.875	93.40	1160	1425	19.33	21.31	6200	− 19
Ce	#	#	#	5.586	—	900	1025	17.80	—	13 100	+ 85
La	#	#	#	6.684	—	1175	1350	30.11	—	9225	− 17
In	#	#	#	5.830	—	1050	1175	17.15	—	5100	− 68
Al	#	#	#	4.230	—	900	1150	13.18	—	3500	+ 12

multiphase compounds.

calculated using the TE_{011} resonant mode of the sample keeping it under the end-shorted condition proposed by Hakki and Coleman [12] and later modified by Courtney [13]. The quality factor was measured by the cavity method [14]. The measurement is made in the transmission mode using the $TE_{01\delta}$ mode. The τ_f was measured by noting the temperature variation of the $TE_{01\delta}$ resonance mode in the temperature range 25–70 °C.

3. Results and discussion

The XRD patterns of ceramics RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] are given in Fig. 1. Brixner [15] made a detailed study on the XRD pattern of rare earth titanium tungstates and molybdates of ABO_4 type and reported that all these materials, except the yttrium compounds, crystallize in the tetragonal scheelite-type structure, while Y($Ti_{0.5}W_{0.5}$)O_4 will crystallize in the monoclinic fergusonite structure. Hence, he indexed RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, and Dy] ceramics comparing with the XRD pattern of $CaWO_4$ [16], which has the tetragonal structure and Y($Ti_{0.5}W_{0.5}$)O_4 by comparing with $YTaO_4$ [17], which crystallizes in the monoclinic form. In the present study, we found that the XRD pattern of Y($Ti_{0.5}W_{0.5}$)O_4 is very similar to that of all other members in the group and hence it was also indexed by comparing with $CaWO_4$ [16], assuming the tetragonal structure for it. Brixner [15] reported that the fergusonite-to-scheelite transition is a reversible one and it may take place in Y($Ti_{0.5}W_{0.5}$)O_4 ceramics at moderate temperatures. It has also been reported [18, 19] that all rare earth niobates with monoclinic structure would transform into the tetragonal scheelite-type structure at moderate temperatures. This transformation might have happened in Y($Ti_{0.5}W_{0.5}$)O_4 since it has sintered at higher temperature (1425 °C/4 h) and hence it seems to be in tetragonal scheelite structure. The XRD patterns given in Fig. 1 are in good agreement with earlier reports [15]. Fig. 2 shows the XRD pattern of ceramics based on Ce, La, Al, and In. The Ce($Ti_{0.5}W_{0.5}$)O_4 does not form and XRD revealed a multiphase compound containing $Ce_2Ti_2O_7$, Ce_2WO_6, TiO_2 and CeO_2 [20]. The XRD patterns of ceramics based on La, Al, and In appear to be very different from each other and also from those of other materials in the rare earth group. It appears that they do not form a single-phase compound.

The lattice parameters and cell volumes of RE($Ti_{0.5}W_{0.5}$)O_4 ceramics are given in Table I. Fig. 3 shows the variation of density and cell volume of these materials with ionic radius [21] of RE^{3+} ions. The bulk density decreases and cell volume increases with increase in ionic radius. The decrease in density is attributed to replacement of RE^{3+} ions by lighter ions and the increase in unit cell volume. Y($Ti_{0.5}W_{0.5}$)O_4

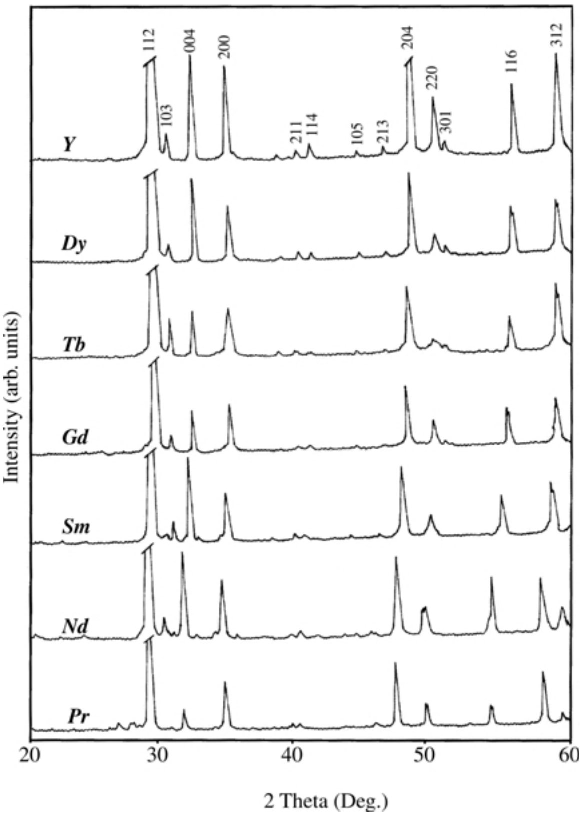

Figure 1 X-ray diffraction pattern of RE($Ti_{0.5}W_{0.5}$)O_4 [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] ceramics.

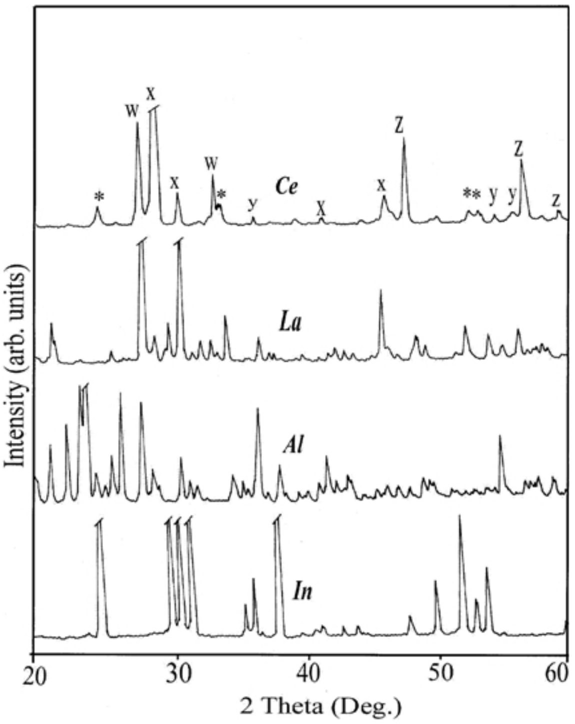

Figure 2 X-ray diffraction pattern of RE_2O_3–TiO_2–WO_3 [RE = Ce, La, Al, and In] ceramics. $w = Ce_2Ti_2O_7$, $x = Ce_2WO_6$, $y = TiO_2$, $z = CeO_2$ and * = Unidentified peaks.

shows some deviation from the group may be due to the fact that it does not belong to the lanthanide group.

Table I gives the preparation conditions, lattice parameters, densities, and microwave dielectric properties of $RE(Ti_{0.5}W_{0.5})O_4$ ceramics. The dielectric constant varies from 13 to 30. The ε_r is maximum for La-based ceramics and minimum for Al-based ceramics. It is well known that some external factors, like porosity, will adversely affect the dielectric constant of a ceramic material. The experimentally observed dielectric constant can be corrected for porosity using the following formula [22].

$$\varepsilon' = \varepsilon_m\left[1 - \frac{3P(\varepsilon_m - 1)}{2\varepsilon_m + 1}\right]$$

where ε' is the dielectric constant (experimental) of the composite sample that contains a porosity P and ε_m is the actual dielectric constant (porosity corrected) of the dielectric material. Fig. 4 gives the variation of experimental (ε_{re}) and porosity-corrected (ε_{rc}) dielectric constant of the ceramics with ionic radius of RE^{3+} ions in $RE(Ti_{0.5}W_{0.5})O_4$ [RE = Pr, Nd, Sm, Gd, Td, Dy, and Y] system. It is evident that the dielectric constant increases almost linearly with ionic radius.

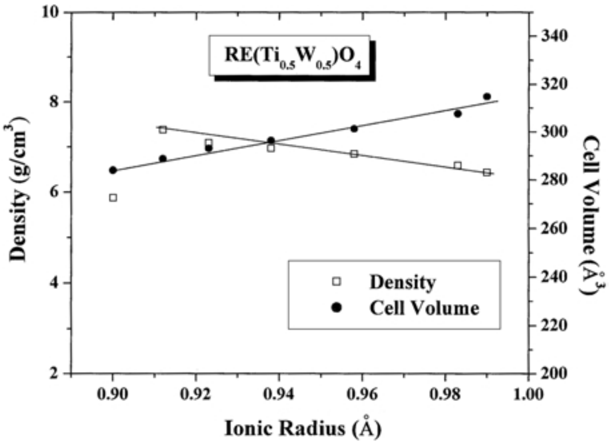

Figure 3 Variation of density and cell volume of $RE(Ti_{0.5}W_{0.5})O_4$ [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] ceramics with ionic radius.

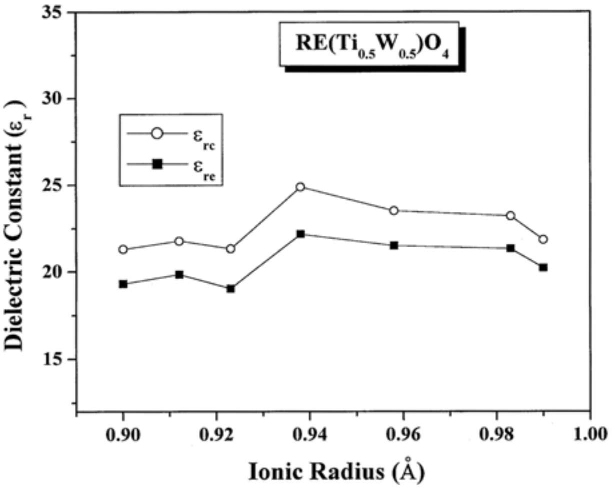

Figure 4 Variation of dielectric constant of $RE(Ti_{0.5}W_{0.5})O_4$ [RE = Pr, Nd, Sm, Gd, Tb, Dy, and Y] ceramics with ionic radius.

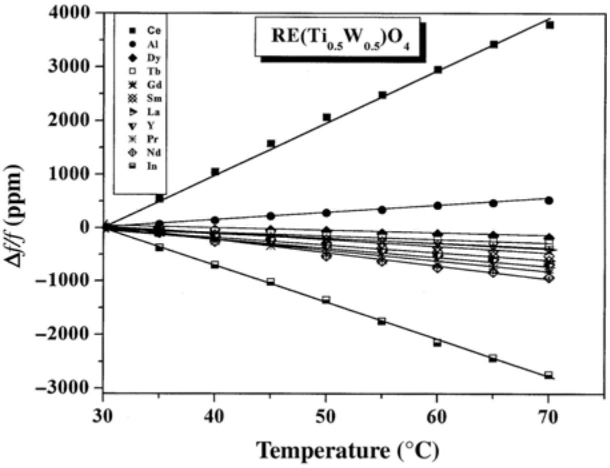

Figure 5 Variation of resonant frequency of $RE(Ti_{0.5}W_{0.5})O_4$ [RE = Pr, Nd, Sm, Gd, Tb, Dy, Y] and Ce-, La-, In-, and Al-based multiphase ceramics with temperature.

The ceramics based on Ce, La, Al, and In do not form a single-phase compound and exhibit some variation from the other members of the group. But they resonated at microwave frequencies and their microwave dielectric properties are also given in Table I. The $RE(Ti_{0.5}W_{0.5})O_4$ [RE = Pr, Nd, Sm, Gd, Td, Dy, and Y] show a low negative value of τ_f The Ce- and Al-based multiphase compounds showed a positive τ_f whereas the La- and In-based multiphase compounds showed a negative τ_f. The variation of resonant frequency with temperature is given in Fig. 5 for different materials from which τ_f was calculated. The quality factor $(Q_u \times f)$ varies from 5000 to 13 000 GHz.

4. Conclusion

Microwave dielectric ceramic materials in the $RE(Ti_{0.5}W_{0.5})O_4$ [RE = Pr, Nd, Sm, Gd, Tb, Dy, and

Y] system have been prepared as single-phase materials by a solid-state ceramic process. Ceramics based on Ce, La, Al, and In were not formed as single-phase compounds. The microwave dielectric properties of all these materials are being reported for the first time. This system includes materials whose dielectric constant varies from 13 to 30, $Q_u \times f$ from 5000 to 13 000 GHz and τ_f from -5 to 85 ppm °C^{-1}. From the measured dielectric properties it can be concluded that the moderate values of ε_r and $Q_u \times f$ restricts the usage of these materials as DRs. But the low τ_f and reasonably good $Q_u \times f$ suggests that there is scope for using these materials in microwave substrate applications. It may be possible to improve their properties by suitable doping and by solid-solution formation.

Acknowledgments

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References

1. D. KAJFEZ and P. GUILLON, in ''Dielectric Resonators'' (Artech House, Massachusetts, 1986).
2. L. A. TRINOGGA, G. KAIZHON and J. C. HUNTER, in ''Practical Microstrip Circuit Design'' (Ellis Horwood, 1991).
3. Y. ISHIKAWA, H. TAMURA, T. NISHIKAWA and K. WAKINO, *Ferroelectrics* **135** (1992) 371.
4. J. TAKAHASHI, K. KAGEYAMA and K. KODARIA, *Jpn. J. Appl. Phys.* **32** (1993) 4327.
5. T. NEGAS, G. YEAGER, S. BELL, N. COATS and I. MINIS, *Am. Ceram. Soc. Bull.* **72**(1) (1993) 80.
6. W. WERSING, ''Electronic Ceramics'', edited by B. C. H. Steele (Elsevier Pub. Co. Inc., 1991) p. 67.
7. P. V. BIJUMON, P. MOHANAN and M. T. SEBASTIAN, *Jpn. J. Appl. Phys.* **41** (2002) (3834).
8. R. RATHEESH, H. SREEMOOLANADHAN, M. T. SEBASTIAN and P. MOHANAN, *Ferroelectrics* **211** (1998) 1.
9. H. SREEMOOLANADHAN, M. T. SEBASTIAN and P. MOHANAN, *Br. Ceram. Trans. J.* **95** (1996) 79.
10. H. M. O'BRYAN, P. K. GALLAGHER, G. W. BERKSTRESSER and C. BRANDLE, *J. Mater. Res.* **5** (1990) 183.
11. N. MCN. ALFORD and S. J. PENN, *J. Appl. Phys.* **80** (1996) 5895.
12. B. W. HAKKI and P. D. COLEMAN, *IEEE Trans. Microw. Theory. Technol.* **MTT-8** (1970) 402.
13. W. E. COURTNEY, *ibid.* **MTT-18** (1970) 476.
14. J. KRUPKA, K. DERZAKOWSKI, B. RIDDLE and J. B. JARVIS, *Meas. Sci. Technol.* **9** (1998) 1751.
15. L. H. BRIXNER, *J. Inorg. Chem.* **3** (1964) 600.
16. JCPDS file card no. 41–1431.
17. JCPDS file card no. 24–1425.
18. R. S. ROTH, in ''Rare Earth Research'' (Macmillan Company, New York, 1961) p. 93.
19. K. A. GINGERICH, in Proceedings of the Annual Conference on ''Applications of X-Ray Analysis'' (Denver, USA, 1963).
20. JCPDS file card nos. 47–67, 30–313, 23–1446, 44–1001.
21. R. D. SHANNON, *J. Appl. Phys.* **73**(1) (1993) 348.
22. S. J. PENN, N. MCN. ALFORD, A. TEMPLETON, X. WANG, M. XU, M. REECE and K. SCHRAPEL, *J. Am. Ceram. Soc.* **80** (1997) 1885.

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