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# Microwave dielectric properties of BaO–2CeO<sub>2</sub>–*n*TiO<sub>2</sub> ceramics

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Received 7 May 2004; received in revised form 28 July 2004; accepted 3 August 2004

Available online 6 October 2004

## Abstract

The BaO–2CeO<sub>2</sub>–*n*TiO<sub>2</sub> ceramics with *n* = 3, 4 and 5 have been prepared with CeO<sub>2</sub> as starting material. The ceramics have been characterized using scanning electron microscopy, X-ray diffraction, Raman and X-ray photoelectron spectroscopy techniques. The microwave dielectric properties have been measured using standard dielectric resonator techniques. BaO–2CeO<sub>2</sub>–3TiO<sub>2</sub> (123), BaO–2CeO<sub>2</sub>–4TiO<sub>2</sub> (124) and BaO–2CeO<sub>2</sub>–5TiO<sub>2</sub> (125) ceramics showed dielectric constants of 38, 27 and 32, respectively. All the ceramics showed fairly good unloaded *Q*-factors. 124 and 125 compounds exhibited low  $\tau_f$  values, while 123 showed a high  $\tau_f$  value  
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**Keywords:** Dielectric resonators; Microwave ceramics; Barium cerium titanates; Low-loss materials

## 1. Introduction

The rapid expansion of telecommunication systems demands dielectric resonators (DRs) as basic components for designing filters and oscillators. Reducing the size is very important for high-quality and low-cost devices. One of the most suitable ways of miniaturizing the filters and reducing their cost is to use high dielectric constant and low-loss ceramic DRs. The important characteristics required for a DR are high  $\epsilon_r$  for miniaturization, high *Q*-factor for selectivity and small temperature variation of the frequency ( $\tau_f$ ) for stability. DRs provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the production of a variety of

microwave devices such as band-selection filters and solid-state oscillators [1,2].

Ceramics in the BaO–*Ln*<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> system [*Ln*=lanthanides such as La, Sm, etc.] have been identified as promising materials for application at frequencies below 2 GHz [3–8]. Many studies [4–8] have proved that these ceramics contained secondary phases like BaTi<sub>4</sub>O<sub>9</sub>, TiO<sub>2</sub>, Ln<sub>2</sub>Ti<sub>2</sub>O<sub>7</sub>, etc. in addition to the major phase, which could be either BaLn<sub>2</sub>Ti<sub>5</sub>O<sub>14</sub> or BaLn<sub>2</sub>Ti<sub>4</sub>O<sub>12</sub> compounds [*Ln*=lanthanides]. It may be noted that in the solid-state mixed oxide preparation method, rare-earth trioxides (Ln<sub>2</sub>O<sub>3</sub>) were used in the raw material stage.

Although many reports have discussed the phase formation, structure, microstructure and dielectric properties of typical BaO–*Ln*<sub>2</sub>O<sub>3</sub>–TiO<sub>2</sub> [*Ln*=rare earth] ceramics, very little attention was paid on Ce-based compounds [3,9–12]. Mudrodubova et al. [3] used Ce<sub>2</sub>O<sub>3</sub> as one of the starting materials. Hoffmann and Waser [9] used chemical method for the preparation of compounds but they decomposed during hot forging.

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Recently, we could succeed in obtaining stable ceramics with BaO–2CeO<sub>2</sub>–5TiO<sub>2</sub> ceramics through solid-state mixed oxide route, which showed interesting microwave DR properties compared to other rare-earth ceramics of the system [12]. In the present paper, we report the preparation and characterization of three different barium–cerium–polytitanate ceramics using CeO<sub>2</sub>.

## 2. Ceramic preparation and characterization

The ceramics were prepared using the conventional mixed oxide route. Starting materials were 99.9% pure BaCO<sub>3</sub>, TiO<sub>2</sub> (Aldrich Chem. Co., USA) and CeO<sub>2</sub> (Indian Rare Earths Ltd., India). Stoichiometric proportions of the above raw materials (1:2:3; 1:2:4; 1:2:5) were mixed in distilled water medium for about 2 h. The three different proportions corresponding to  $n = 3, 4$  and 5 are hereafter referred to as 123, 124 and 125. Each part was separately dried and calcined at 1150–1200 °C for 4 h in air. The powder was ground thoroughly for about 2 h and then cold pressed in a WC die of diameter 11 mm under 200 MPa pressure. The pellets were then sintered at 1225–1275 °C for 4 h in air.

Sintered specimens were polished and bulk densities were measured. Selected pellets were etched and the surface is examined under scanning electron microscope (SEM). X-ray diffraction (XRD) patterns were recorded with powders of thin compacts using CuK $\alpha$  radiation in the 20–60° 2 $\theta$  range.

The dielectric constant ( $\epsilon_r$ ), quality factor ( $Q$ ) and temperature variation of resonant frequency ( $\tau_f$ ) were measured using cylindrical specimens.  $\epsilon_r$  and  $\tau_f$  were calculated from the frequency of TE<sub>011</sub> mode of the specimens under end-shortened condition [13].  $\tau_f$  was measured by noting the variation of resonant frequency as a function of temperature in the range 25–75 °C.  $Q$  was calculated from the transmission coefficient of the band-rejection filter incorporating the specimens [14].

X-ray photoelectron spectra (XPS) have been recorded using a PHI 5600 ci multitechnique spectrometer.

The base pressure during the experiment was about  $5 \times 10^{-10}$  Torr. All the spectra were recorded using monochromatic AlK $\alpha$  X-rays (1486.6 eV) with a full-width at half-maximum of 0.3 eV. The ceramic specimens were sliced with a specially designed crystal cleaver under ultrahigh vacuum conditions. This type of sample preparation is used to obtain contamination-free surfaces so that the study of the intrinsic properties of the samples is not disturbed by adsorbents like carbon.

Raman spectra of the powdered samples were measured with a Dilor XY-800 spectrometer that was equipped with a charge-coupled device camera. The setup was coupled with a neodymium yttrium vanadate (Nd:YVO<sub>4</sub>) laser (Spectra Physics: Millennia V,  $\lambda = 532$  nm). The continuous wave output power of this laser was typically 100 mW during the experiments. The slit width of the Raman spectrometer was set to 100  $\mu$ m, so that the resulting energy resolution was 0.7 cm<sup>-1</sup>. Scattered light was detected both in back-scattering and 90° configuration.

## 3. Results and discussion

During our studies [5,8] of the lanthanide ceramics of 123, 124 or 125 compositions, DRs of diameter 9–10 mm and thickness 5–7 mm showed fundamental resonances in S-band region. But, all specimens in the present composition with same dimensions showed fundamental resonance in the C-band region. The dielectric properties of BaO–2CeO<sub>2</sub>– $n$ TiO<sub>2</sub> ceramics are given in Table 1. They have  $\epsilon_r$  38, 27 and 32 for 123, 124 and 125 ceramics, respectively, at 5–6 GHz. It is interesting to note that the  $\epsilon_r$  values of all the cerium-containing polytitanate analogs [5–10]. Fig. 1 shows the variation of resonant frequencies of these ceramic DRs with temperature. The 124 ceramic has the lowest value of  $\tau_f$  (+9 ppm/C) and 123 ceramic has the highest value (+159 ppm/C). The  $\tau_f$  value of 125 ceramic is +41 ppm/C and is in good agreement with the  $\tau_f$  values measured earlier using different WG modes [12]. These

Table 1  
Microwave dielectric properties of barium–rare earth–polytitanates

Ceramics	$\epsilon_r$	Qxf (GHz)	$\tau_f$ (ppm/°C)	$\rho$ (g/cm <sup>3</sup> )	Remarks
BaO–Nd <sub>2</sub> O <sub>3</sub> –3TiO <sub>2</sub>	60	5360	140	5.4	Ref. [5]
BaO–2CeO <sub>2</sub> –3TiO <sub>2</sub>	38	7200	159	4.6	This work
BaO–La <sub>2</sub> O <sub>3</sub> –4TiO <sub>2</sub>	89	1900	301	4.9	Ref. [10]
BaO–2CeO <sub>2</sub> –4TiO <sub>2</sub>	27	18560	9	5.01	This work
BaO–Pr <sub>2</sub> O <sub>3</sub> –4TiO <sub>2</sub>	91	5600	135	5.5	Ref. [10]
BaO–Nd <sub>2</sub> O <sub>3</sub> –4TiO <sub>2</sub>	84	6190	68	5.0	Ref. [5]
BaO–La <sub>2</sub> O <sub>3</sub> –5TiO <sub>2</sub>	85	2800	345	4.9	Ref. [10]
BaO–2CeO <sub>2</sub> –5TiO <sub>2</sub>	32	19100	41	5.1	This work, Ref. [12]
BaO–Pr <sub>2</sub> O <sub>3</sub> –5TiO <sub>2</sub>	78	7090	147	5.3	Ref. [10]
BaO–Nd <sub>2</sub> O <sub>3</sub> –5TiO <sub>2</sub>	78	4620	40	5.1	Ref. [5]

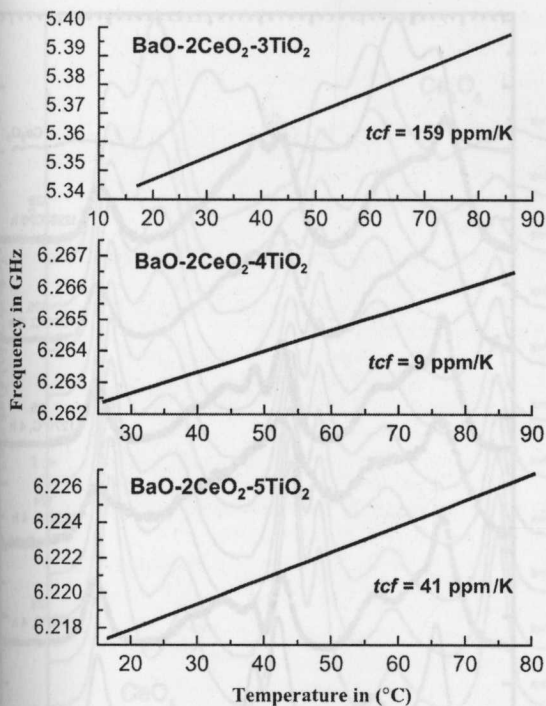


Fig. 1. Variation of resonant frequency with temperature.

differences in the  $\tau_f$  values between the different compositions are due to differences in the temperature variation of dielectric constant ( $\tau_\epsilon$ ) and coefficient of thermal expansion ( $\alpha$ ), i.e.,

$$\tau_f = -\alpha - \tau_\epsilon/2.$$

Conventional rare-earth polytitanate ceramics show high positive  $\tau_f$  in the microwave range. Since Ce is between La and Pr in the periodic table, one would expect the cerium analogs to show relatively high  $\tau_f$ . But, it can be seen that  $\tau_f$  of 125 ceramic as well as 124 ceramic are small and that of 123 ceramic is high. There exist vast differences between conventional rare-earth polytitanates and ceria compounds in dielectric properties. This shows that the phase constitution of these ceramics must be totally different from the BaO-RE<sub>2</sub>O<sub>3</sub>-*n*TiO<sub>2</sub> phases formed with other rare-earth compounds. However, the ceramics showed excellent sinterability with low porosity. Fig 2 shows the SEM pictures recorded from thermally etched surface of samples. The photographs are similar with grain size up to  $\sim 10\mu$ . The 124 ceramic shows elongated grains which indicate presence of secondary phase.

Powder XRD patterns of Ce-based ceramics, recorded using CuK $\alpha$  radiation, are shown in Fig. 3. The patterns are very much different from that of the conventional BaO-RE<sub>2</sub>O<sub>3</sub>-*n*TiO<sub>2</sub> compounds [3–5]. The latter possess tungsten-bronze type orthorhombic unit cell structure. Since there are no ternary single-phase compounds in the BaO-CeO<sub>2</sub>-TiO<sub>2</sub> system near these

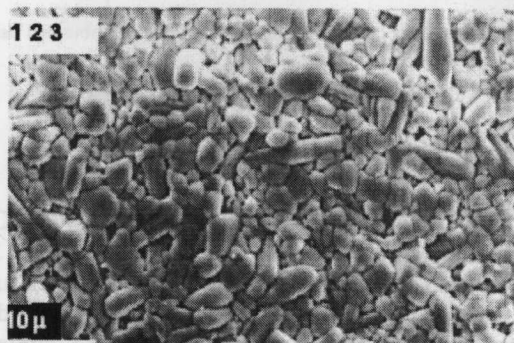
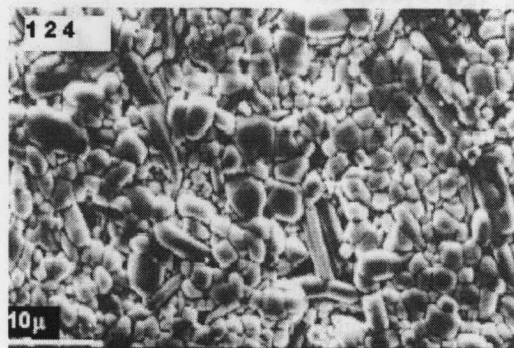


Fig. 2. SEM photographs of BaO-2CeO<sub>2</sub>-*n*TiO<sub>2</sub> ceramics.

ratios [11], the patterns could not be indexed based on any available standard JCPDS pattern. Guha [14] also did not report any single-phase compounds with these stoichiometries in his study of the BaO-CeO<sub>2</sub>-TiO<sub>2</sub> system. The phase diagrams of BaO-*Ln*<sub>2</sub>O<sub>3</sub>-*n*TiO<sub>2</sub> (*Ln*=rare earth like La, Nd; *n*= 3, 4, 5) compounds have been studied in detail by many researchers [3,9,15,16]. Those reports showed that cerium (*Ln*=Ce) would not come under this phase diagram because of the 4<sup>+</sup> valence.

The dielectric properties and the XRD patterns of CeO<sub>2</sub>-based compounds differ remarkably from other lanthanide analogs. If CeO<sub>2</sub> had completely converted to Ce<sub>2</sub>O<sub>3</sub>, the dielectric properties and XRD would have matched with other lanthanide analogs. Hence, we carried out XPS study to examine the valence state of cerium ion in these compounds.

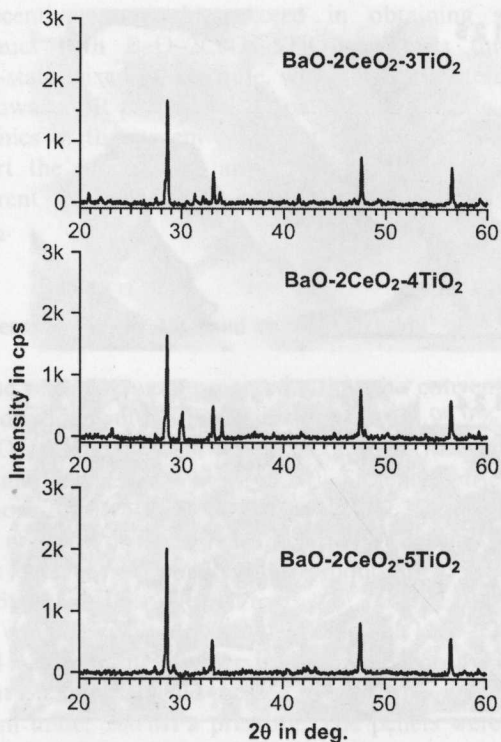


Fig. 3. XRD patterns of BaO–2CeO<sub>2</sub>–*n*TiO<sub>2</sub> ceramics obtained using CuK $\alpha$  radiation.

#### 4. X-ray photoelectron spectroscopy (XPS)

We have performed XPS studies to quantify the Ce ion formation. First, photoelectron spectra of the Ce 3d levels in pure CeO<sub>2</sub> [17] and Ce<sub>2</sub>O<sub>3</sub> [18] were taken and compared with that of the ceramics (see Fig. 4). In order to accurately estimate the percentage of Ce<sub>2</sub>O<sub>3</sub> content in these samples, spectra of pure CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub> were plotted, superimposed for mixtures (1–*x*)CeO<sub>2</sub> + *x*Ce<sub>2</sub>O<sub>3</sub> to get a series of spectra (see Fig. 5) and compared with the 3d XPS spectra of the studied ceramics. The metric distances were derived between the measured Ce 3d XPS spectra and the superimposed ones. With respect to the distance, the square root of standard deviation was determined. The normalized distance is defined as

$$D_{\text{RMS}}(f, g) = \frac{1}{\sqrt{2}} \sqrt{\sum_i^n \left( \frac{f_i}{|f|} - \frac{g_i}{|g|} \right)^2},$$

where  $f_i$  and  $g_i$  denote the  $i$ th point of the measured spectrum  $f$  and the synthesized (calculated) spectrum  $g$ , respectively. The minimum of the resulting values denoted the best agreement between the measured spectrum and the series of the synthesized spectra. In Ba–Ce compounds Ce 3d peaks in the XPS spectra are overlapped by Barium MNN Auger peaks if AlK $\alpha$

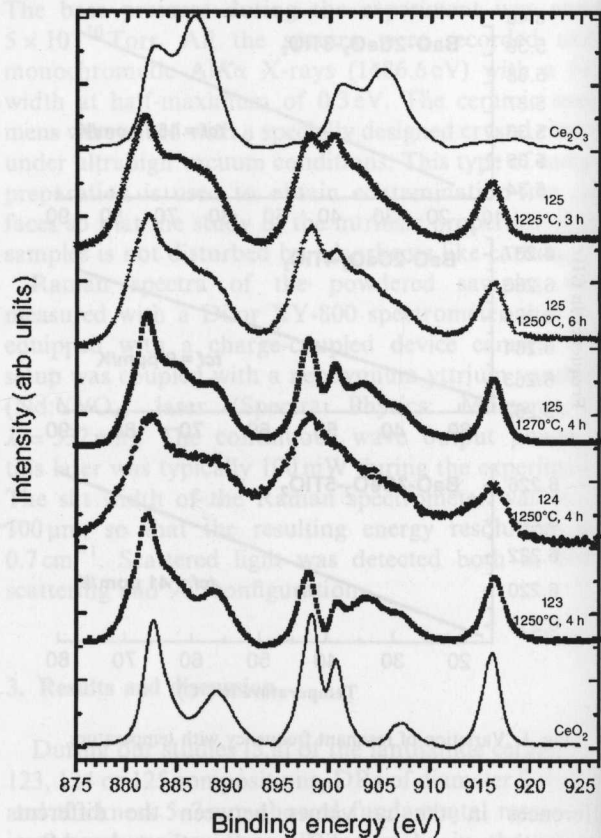


Fig. 4. XPS spectra of BaO–2CeO<sub>2</sub>–*n*TiO<sub>2</sub> ceramics along with that of CeO<sub>2</sub> and Ce<sub>2</sub>O<sub>3</sub>.

radiation is used for excitation. Therefore, Ba MNN has been measured in a BaTiO<sub>3</sub> single crystal. After subtracting the inelastic background from all obtained spectra using the Tougaard method [19], the Ba MNN could be normalized to the Ba 3d peak intensity. Finally, the Ba MNN could be subtracted.

The spectra of the ceramics in Fig. 4 show that they contained Ce<sup>3+</sup>. We first compared the patterns obtained for ceramic 125 at 1225°C with the superimposed patterns. Best matching obtained with that of {35% Ce<sub>2</sub>O<sub>3</sub> + 65% CeO<sub>2</sub>}. This meant that 35% of Ce atoms in the ceramic sample existed as Ce<sup>3+</sup> whereas 65% remained in the Ce<sup>4+</sup> state. Similar analyses were performed with ceramics 123 and 124 also. The amounts of Ce<sub>2</sub>O<sub>3</sub> in these samples were found to be 35% and 45%, respectively.

In order to study the change in valence of Ce atoms with respect to the synthesis conditions, XPS measurements were carried out with three different 125 samples sintered in air at 1225, 1250 and 1270°C (see Fig. 4). As the sintering temperature increases, slight changes could be seen in the spectral features. We calculated the amount of Ce<sub>2</sub>O<sub>3</sub> in different processing temperatures as

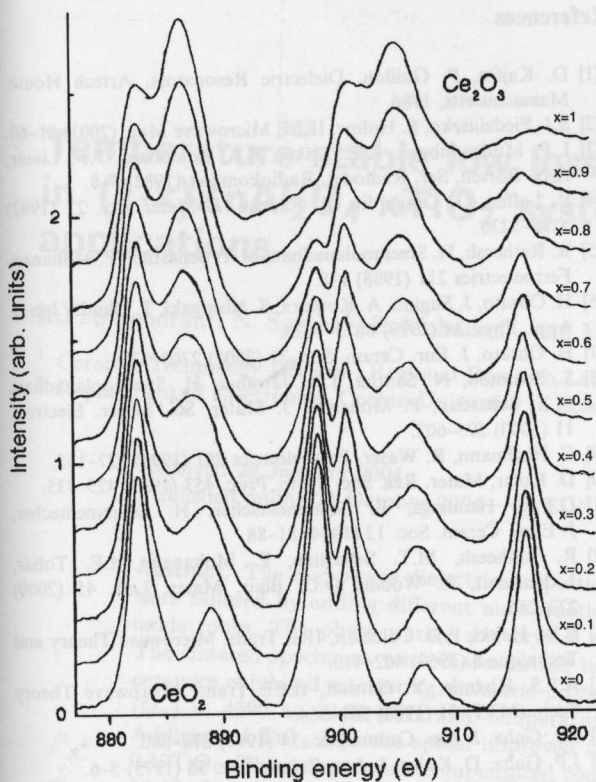


Fig. 5. XPS spectra of pure  $\text{CeO}_2$  and  $\text{Ce}_2\text{O}_3$  and superimposed mixtures  $(1-x)\text{CeO}_2 + x\text{Ce}_2\text{O}_3$ .

well and results are compiled in Table 2. It can be seen that as the sintering temperature increases, there is no marginal change in the amount of  $\text{Ce}_2\text{O}_3$  in the sample. At 1270 °C, the sample started melting. So the estimated maximum amount of  $\text{Ce}_2\text{O}_3$  content in these ceramics is around 40% near the melting point. The compounds can be slightly non-stoichiometric due to the existence of Ce in +3 and +4 states. However, they showed good microwave dielectric properties.

Kolar [10] in his work on  $\text{CeO}_2$ – $\text{BaTiO}_3$  solid solution, showed that in presence of excess  $\text{TiO}_2$ , cerium could be reduced even in air and enter at  $\text{Ba}^{2+}$  site of  $\text{BaTiO}_3$  as  $\text{Ce}^{3+}$ . He showed that when  $\text{TiO}_2:\text{CeO}_2 > 3:4$ , the compound formed would be  $(\text{Ba}_{0.45}\text{Ce}_{0.55})(\text{Ti}_{0.55}^{4+}\text{Ti}_{0.45}^{3+})\text{O}_3$ . He arrived at this formula using wavelength dispersive spectroscopy on a sample whose initial stoichiometry was  $\text{BaO}$  (20 mol%) +  $\text{CeO}_2$  (30 mol%) +  $\text{TiO}_2$  (50 mol%). This composition is near our present 123 ceramic, which is 16.7:33.3:50. Other ceramics are quite different from this. Kolar processed the ceramics near 1400 °C where  $\text{Ti}^{4+}$  to  $\text{Ti}^{3+}$  conversion is effective. In this work, the processing temperatures were below 1300 °C and  $\text{Ti}^{3+}$  formation is trivial. Hennings et al. [11] showed that  $\text{Ce}^{4+}$  can substitute in the  $\text{Ti}^{4+}$  site in their studies on  $\text{CeO}_2$ – $\text{BaTiO}_3$  ceramics. Thus, even if

Table 2  
Estimation of  $\text{Ce}^{3+}$  content in  $\text{BaO}$ – $2\text{CeO}_2$ – $n\text{TiO}_2$  ceramics

Sample	Sintering temperature (°C)	Amount of $\text{Ce}^{3+}$ (%)
125	1225	35
	1250	35
	1270	40
124	1250	35
123	1250	40

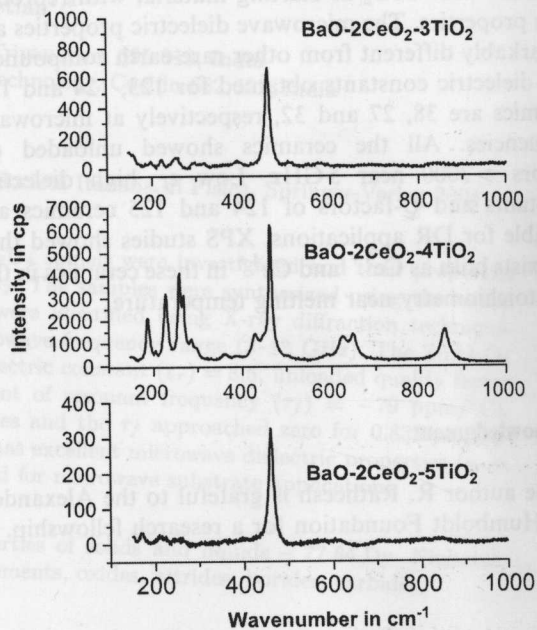


Fig. 6. FT Raman spectra of  $\text{BaO}$ – $2\text{CeO}_2$ – $n\text{TiO}_2$  ceramics.

$\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  are present, they could substitute for  $\text{Ba}^{2+}$  and  $\text{Ti}^{4+}$  sites in the stoichiometry near  $\text{BaTiO}_3$ . As in this work, the stoichiometry is far above this, a clear result of phase constitution is not possible easily. However, effort is in progress to identify the constituents.

FT Raman spectra of these ceramics were obtained to get an idea about the overall symmetry of these compounds and are shown in Fig. 6. It can be seen that the spectra of 123 and 125 ceramics are similar with a strong peak in the 400–500  $\text{cm}^{-1}$  region along with very weak features in the 150–300  $\text{cm}^{-1}$  region. But, the spectrum of 124 ceramic shows strong peaks in the 100–400  $\text{cm}^{-1}$  region in addition to the strong one at around 475  $\text{cm}^{-1}$ . The strong mode observed in all the three compounds in the 450–500  $\text{cm}^{-1}$  region is assigned to the symmetric stretching vibrations ( $\nu_1$ ) of the  $\text{TiO}_6$  octahedra. The Raman active symmetric bending vibrations of these compounds are observed as medium intense bands in the 180–270  $\text{cm}^{-1}$  region. In the case of

124, two medium broadbands also appeared at around 650 and 875  $\text{cm}^{-1}$ . It can be inferred from the spectra that the symmetry of 123 and 125 ceramics is higher compared to that of 124 ceramic.

## 5. Conclusion

$\text{BaO}-2\text{CeO}_2-n\text{TiO}_2$  ( $n = 3, 4$  and  $5$ ) ceramics can be obtained with  $\text{CeO}_2$  as starting material with reproducible properties. The microwave dielectric properties are remarkably different from other rare-earth compounds. The dielectric constants obtained for 123, 124 and 125 ceramics are 38, 27 and 32, respectively at microwave frequencies. All the ceramics showed unloaded  $Q$ -factors  $>2000$  near 5 GHz. Low  $\tau_f$ , high dielectric constants and  $Q$ -factors of 124 and 125 ceramics are suitable for DR applications. XPS studies showed that Ce exists both as  $\text{Ce}^{3+}$  and  $\text{Ce}^{4+}$  in these ceramics in the 4:6 stoichiometry near melting temperature.

## Acknowledgment

The author R. Ratheesh is grateful to the Alexander von Humboldt Foundation for a research fellowship.

## References

- [1] D. Kajfez, P. Guillon, Dielectric Resonators, Artech House, Massachusetts, 1986.
- [2] S.J. Fiedziuszko, S. Holme, IEEE Microwave Mag. (2001) 51–60.
- [3] L.P. Mudrodubova, K.E. Lisker, B.A. Totenberg, T.F. Limar, A.N. Borsch, Ser. Radiodet. Radiokomp. 1 (1982) 3–8.
- [4] P. Laffez, G. Desgardin, B. Raveau, J. Mater. Sci. 27 (1992) 5229–5238.
- [5] R. Ratheesh, H. Sreemoolanadhan, M.T. Sebastian, P. Mohanan, Ferroelectrics 211 (1998) 1–8.
- [6] H. Ohsato, J. Sugino, A. Komura, S. Nishigaki, T. Okuda, Jpn. J. Appl. Phys. 38 (1999) 5625–5628.
- [7] H. Ohsato, J. Eur. Ceram. Soc. 21 (2001) 2703–2711.
- [8] S. Solomon, N. Santha, I.N. Jawahar, H. Sreemoolanadhan, M.T. Sebastian, P. Mohanan, J. Mater. Sci. Mater. Electron. 11 (2000) 595–602.
- [9] C. Hoffmann, R. Waser, Ferroelectrics 201 (1997) 127–135.
- [10] D. Kolar, Mater. Res. Soc. Symp. Proc. 453 (1997) 425–435.
- [11] D.F.K. Hennings, B. Schreinemacher, H. Schreinemacher, J. Euro. Ceram. Soc. 13 (1994) 81–88.
- [12] R. Ratheesh, M.T. Sebastian, P. Mohanan, M.E. Tobar, J. Hartnett, R. Woode, D.G. Blair, Mater. Lett. 45 (2000) 279–285.
- [13] B.W. Hakki, P.D. Coleman, IRE Trans. Microwave Theory and Technique 8 (1960) 402–410.
- [14] A.P.S. Khanna, Y. Garault, IEEE Trans. Microwave Theory Tech. (MTT) 31 (1983) 261–264.
- [15] J.P. Guha, J. Am. Ceram. Soc. 74 (1991) 878–880.
- [16] J.P. Guha, D. Kolar, J. Am. Ceram. Soc. 56 (1973) 5–6.
- [17] L. Douillard, M. Gautier, N. Thromat, M. Henriot, M.J. Guittet, J.P. Duraud, F. Tourillon, Phys. Rev. B 49 (1994) 16171–16180.
- [18] J.G. Clabes, J. Vac. Sci. Technol. A 6 (1988) 2887–2892.
- [19] S. Tougaard, P. Sigmund, Phys. Rev. B 25 (1982) 4452–4466.