Structural, optical and microwave dielectric properties of barium tetra titanate ($BaTi_4O_9$) ceramics

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Ceramic composition of Barium tetra titanate ($BaTi_4O_9$) is prepared via conventional solid state, mixed oxides route.The XRD revealed a single phase orthorhombic (Amm2)structured $BaTi_4O_9$compound calcined at 1250 °C for 2 h in air. Thevalues of the relative permittivity (ε_r) varied from~38 to 43 and quality factor ($Q \times f$) *from*~27000 to 39000 GHzat 3 GHz frequency with increasing sintering temperatures ranging from 1500 °C to 1580 °C in air. The microwave dielectric properties of the sintered ceramicsample depend considerably on sintering temperature and their microstructure. $BaTi_4O_9$ can be a promising microwave dielectric material for microwave applications.

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1. Introduction

Barium titanate ($BaTiO_3$) and Barium tetratitanate ($BaTi_4O_9$) are candidate materials for dielectric resonators in microwave telecommunication and satellite broadcasting Devices [1]. Functioning as important components in communication circuits, dielectric resonators can create, filter and select frequencies in oscillators, amplifiers and tuners. Microwave dielectric resonators provide significant advantages in terms of compactness, light weight, temperature stability and relatively low cost in the fabrication of higher frequency devices. The characteristics required for dielectric resonators are, in general, (a) high dielectric constant or relative permittivity (ε_r) to achieve miniaturization of components in view of ($1/\ \varepsilon_r^2$) size dependence, (b) high quality factor ($Q \times f$) value to minimize microwave dielectric loss and (c) smaller temperature coefficient of resonant frequency (τ_f) for frequency stabilization. $BaTi_4O_9$ meet these requirements effectively having ε_r = 39, $Q \times f$ = 10,000 GHz and τ_f = 14 ppm/°C [1]. However, the fabrication of monophasic ceramics is required to obtain the desirable dielectric characteristics. Therefore, the synthesis of monophasic titanates has been a subject of several investigations. The conventional solid-state reaction route, involving high temperature sintering of homogeneous mixtures of $BaCO_3$ and TiO_2, may also result in the formation of secondary phases unless the synthetic parameters are precisely controlled as there are several thermodynamically stable compounds in the vicinity of the desired composition of theTiO_2rich part of the $BaTiO_3$system [2–4]. Moreover, the ceramics may get contaminated with impurities from the grinding media. Nagas et al[5] have described the detrimental effects of other barium titantes and impurities on the dielectric behavior of barium titantes and barium tetra titanates. In view of these limitations, attempts have been made to synthesize the ceramics with improved phase purity as well as dielectric properties using different additives [6-8]. On the other hand, wet chemical routes such as co-precipitation, sol–gel or combustion that provide an intimate blending of the constituents have also been employed to synthesize the titanates[9].

The present report describes the preparation of $BaTi_4O_9$ ceramics by mixed oxide route. The powders and sintered products obtained were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM) and Fourier transformed infra-red radiation (FTIR) spectroscopy. The dielectric properties of the ceramics are discussed in terms of their physical and chemical characteristics.

2. Experimental procedures

The solid solution of barium tetra titanate ($BaTi_4O_9$) material was obtained by mixed oxides solid state reaction route. High purity starting materials: barium carbonate ($BaCO_3$, purity 99.9%) and titanium dioxide (TiO_2, purity 99.9%) (Aldrich Chemicals) were mixed accordingly to stoichiometric ratio. The mixture of raw powders were ground in distilled water (wetting media) for 24 h in a horizontal ball mill with zirconia balls of 5 mm as a grinding media. The prepared powders were dried in oven at 90 °C for 24 h in air. The dried mixture was calcined in high purity alumina crucible at 1250 °C for 2 h in air with 5 °C/min of heating/cooling rate in a conventional furnace. The calcined mixture was grinded manually with a pistol and mortarfor to avoid agglomeration. The fine powder was pressed into pellets of 10 mm in diameter and 5 mm

thick under a pressure of 100 MPa using a manual pellet press (CARVER, USA). The pellets samples were sintered at various temperatures ranging from 1500 °C to 1580 °C in air in air with heating/cooling rates of 5 °C/min. The crystalline phases of the calcined $BaTi_4O_9$ sample ceramic was identified by using X-rays diffractometer (XRD) (JDX-3532, JEOL, Japan) with Cu Kα (λ = 0.15406 nm) radiation operated at 40 mA and 40 kV in a wide range of Braggs angles 2θ (10° < 2θ < 90°) at scanning rate of 2°/min. The apparent bulk density and microstructural information was obtained by the Archimedes principle and SEM (JSM-5910, JEOL Japan) respectively. The Fourier transform infra-red radiation (FTIR) absorption spectrum was recorded on a Perkin-Elmer GX FTIR system was used to obtain 10 cm^{-1} resolution spectrum in the range 400 to 4000 cm^{-1} region. The photoluminescence (PL) spectrum was recorded on a JobinYvon-Horiba Triax 190 spectrometer with 0.30 nm resolution spectrum. The dielectric properties of sintered ceramic sample were measured by using Impedance Analyzer (Agilent-E4991A, 1MHz-3GHz).

3. Results and discussions

3.1. Structural analysis

Fig. 1 shows the XRD patterns of the barium tetra titanate($BaTi_4O_9$) calcined ceramic at 1250 °C for 2 h in air. The XRD patterns shows the orthorhombic structure of $BaTi_4O_9$ matched with JCPDS card # 34-70 and subsequently lattice parameters were observed. The lattice parameters (a = 0.39828(3) nm, b = 0.56745(5) nm, c = 0.56916(5) nm) and lattice volume (V = 0.0643 nm^3) with space group Amm2 (38) for $BaTi_4O_9$ ceramic material was measured using Win XPow software. The crystallite size of each plan can be determined by using the Debye Scherer's formula [10] and recorded 11.0 nm average crystallite size as shown in Table 1.

$$D = \frac{0.9\lambda}{\beta Cos\theta} \quad (1)$$

where 'D' is the crystallite size, 'λ' is the wavelength of Cu Kα radiation, 'θ' is the brags angle and 'β' is the full-width at half-maximum (FWHM). The average crystallite size of $BaTi_4O_9$ sample was reported to be 15.0 nm [11].

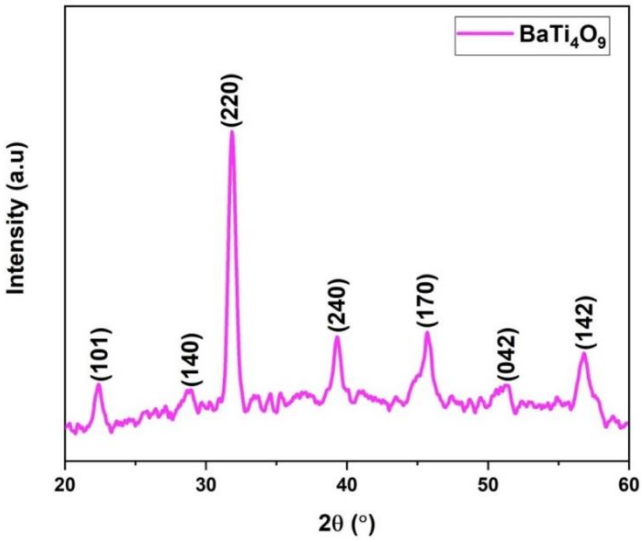

Fig. 1. XRD pattern of $BaTi_4O_9$ calcined ceramic at 1250 °C for 2 h in air (color online)

Table 1. Crystallite size of each plane

Planes	Brags angle (2θ) (degree)	Brags angle (θ) (degree)	FWHM (β) (degree)	FWHM (β) (radian)	Crystallite size (D) (nm)
(101)	22.38	11.19	0.67	0.0117	12.05
(140)	28.79	14.40	0.58	0.0101	14.15
(220)	31.86	15.93	0.62	0.0108	13.33
(240)	39.39	19.69	0.82	0.0144	10.23
(170)	45.61	22.81	1.22	0.0212	7.10
(042)	51.02	25.51	1.03	0.0180	8.54
(142)	57.84	28.92	0.83	0.0145	10.93

3.2. Microstructure analysis

The secondary electron SEM images (SEIs) with different resolutions, from thermally etched and gold-coated $BaTi_4O_9$ceramic sample sintered at 1500 °C/2h is shown in Fig 2. The sintered microstructure of the sample consisted in average grain size ~7×1 $\mu m^2$and with the apparent density (5.630 $gmcm^{-3}$), calculated density (5.502 $gmcm^{-3}$) and relative density is (97.72 %).

The relative densities of barium tetra titanates prepared by other wet chemical methods or mixed oxide route often range within 84–96% [12-14]. Negligible porosity has seen in $BaTi_4O_9$ sample due to higher relative density. Porosity can be decreases by increasing the relative density above 90 % [15].

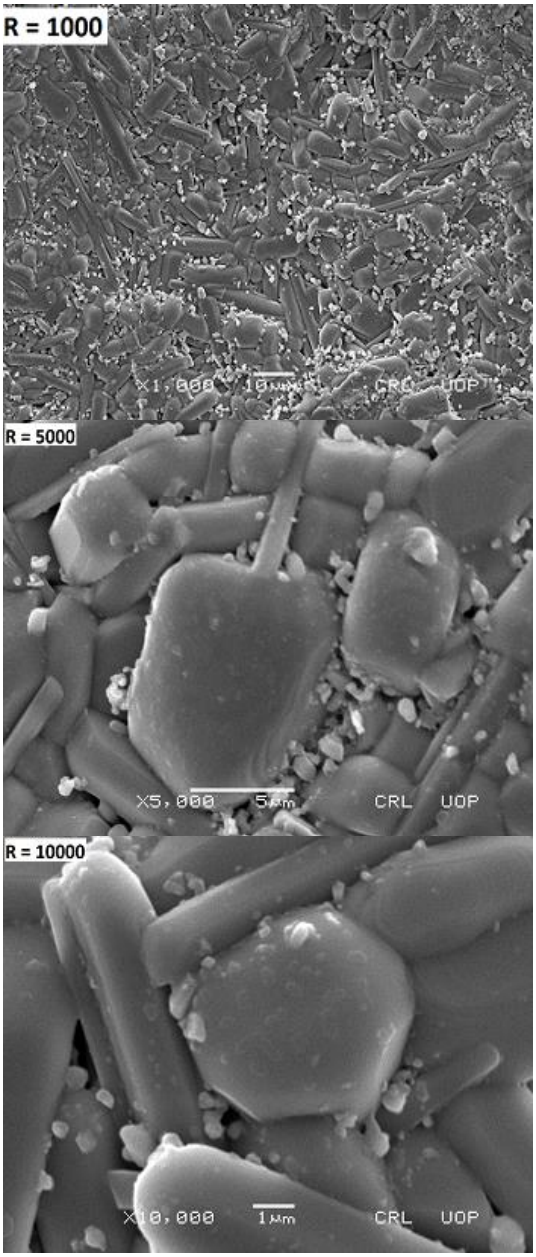

Fig. 2. SEM images from thermally etched and gold coated surfaces of $BaTi_4O_9$ sintered ceramic at 1500 °C for 2 h

3.3. Optical properties

Fig. 3 shows the FTIR pattern of fabricated compound $BaTi_4O_9$ ceramic material. FTIR spectrum of sample is displays many type of vibrations at 469, 507, 832, 855, 1436, 1713, 2853 and 2924 cm^{-1} and they were assigned to the stretching of Ti-O and Ba-O respectively. A broad band centered at 1436 cm^{-1} was assigned to the stretching and in-plane deformation mode. Several vibrations modes were observed in the FTIR spectrum. Therefore, the comparative study of the FTIR spectra further supports the improvement of redispersibility of the crystalline barium tetra titanatedielectric material.

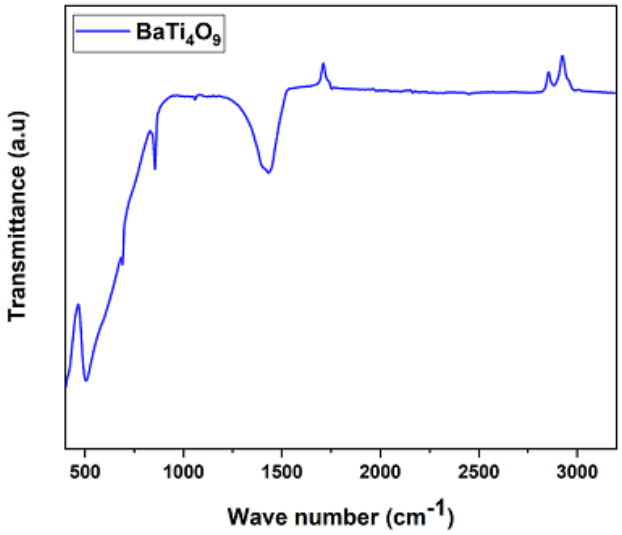

Fig. 3. FTIR spectrum of$BaTi_4O_9$ calcined powder at 1250 °C for 2 h (color online)

Photoluminescence (PL) spectrum of $BaTi_4O_9$ ceramic material excited with 488 nm laser beam source at room temperature shown in Fig. 4. PL spectrum of $BaTi_4O_9$ dielectric material have defected related deep level emission in the visible region of the optical spectrum. The emission in the visible region is recognized to the recombination of holes and electron in the state of delocalization. This state of delocalization is due to the intrinsic structural defect related to Ti^{4+} microcrystal symmetric in the micro phase of $BaTi_4O_9$. The PL emission spectrum of the sample is recorded red color (605 nm) with excitation energy (2.05 eV).

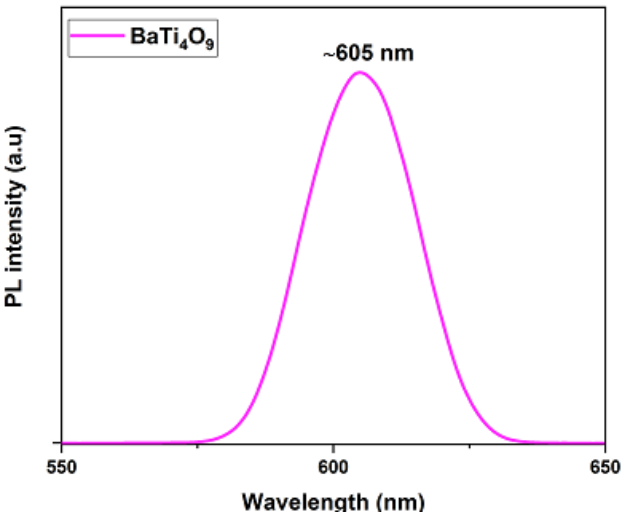

Fig. 4. PL spectrum of$BaTi_4O_9$ calcined powder at 1250 °C for 2 h (color online)

This red color represented the electronic transition generated by different degree of structural order-disorder in sample [16]. PL is a typical multiphoton process that is an emission occurred in optical energy gape by many vibrational stats within it. This can confirmed that PL is directly associated with the existing localized state within

the band gape which affected the structural order-disorder directly. Therefore, the structural order increases with increasing the band gape energy. It is observed that a broad emission band is located at ~605 nm have excitation energy (~2.05 eV) are smaller than the band gap energy of highly ordered barium tetra titanate located at ~558 nm (~2.23 eV) which is due to the oxygen vacancy [17]. In this PL characteristics oxygen vacancy act as a red color emitted source.

3.4. Microwave dielectric properties

The microwave dielectric properties of $BaTi_4O_9$sintered ceramic sample at 1500 °C for 2 h have been investigated. The variations of dielectric constant or relative permittivityand dielectric loss were consistent with frequency as shown in the Fig. 5. Vikram S Yadav and M.T Sebastian reported that the dielectric constant and dielectric loss of the resonators affected by the microwave frequencies and sintering temperature as well. The origin of dielectric losses can also be considered as being related to delay between the electric field and the electric displacement vectors[18, 19].We have observed that the dielectric constant increases after 800 MHz frequency while dielectric loss of barium tetra titanate ceramic decreases. Soaking time and sintering temperature also affected the dielectric properties of sample. Accordingly, dielectric properties have dependence on the lattice vibration mode, ionic polarization, porosity, bulk density as well as grain morphology [20].

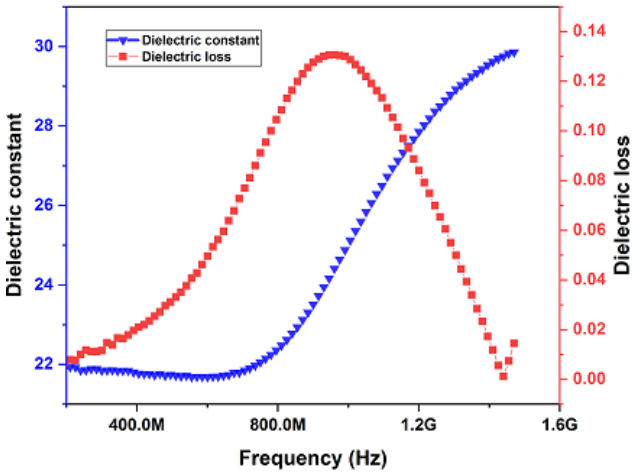

Fig. 5. Variation of dielectric constant and dielectric loss vs frequencies of $BaTi_4O_9$ sintered ceramic at 1500 °C for 2 h (color online)

Fig. 6 shows the variation of relative permittivity and quality factor of $BaTi_4O_9$ sintered ceramic sample versus sintering temperatures. These dielectric properties increase with increasing sintering temperature.We have observed high dielectric constant (43) and good quality factor (39000 GHz) at relatively 3GHz frequency. Ting Luo et al reported that dielectric constant is (36.9), quality factor (7800 GHz) and temperature coefficient of resonant frequency (14 ppm/°C) [21].

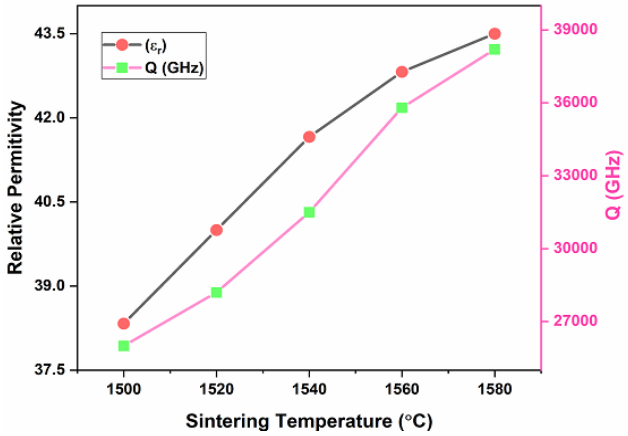

Fig. 6. Variation of relative permittivity and quality factor vs sintering temperatures of $BaTi_4O_9$ sintered ceramic sample (color online)

4. Conclusions

In the present work, we have synthesized barium tetra titanate($BaTi_4O_9$) ceramic material by conventional mixed oxide route without using any stabilizing agent and studied the effect of sintering temperature on their microwave dielectric properties. The phase content of sintered ceramic shows a subtle variation on the relative concentration of Ba and Ti in the starting materials. The $BaTi_4O_9$ ceramic sample showed dense microstructure, high dielectric constant (43) andgood quality factor(39000 GHz).

Acknowledgments

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