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Structural, Dielectric and Ferroelectric Properties of Tungsten Substituted Barium Titanate Ceramics

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In the present work, X- ray diffractograms analysis reveals the formation of the single phase crystalline structure. Tetragonal strain of the samples have been calculated and it shows a decrease with increasing sintering temperature. The variation of dielectric constant (ε_r) with temperature shows that the samples undergo a diffuse type ferro - paraelectric phase transition. The dielectric constant is found to increase with increasing sintering temperature. Variation of dielectric loss (tanδ) with temperature have also been measured. Further, the diffusivity of the samples has been calculated and is reported in this paper. The P-E studies of the W-substituted barium titanate ceramics with temperatures are reported.

Key Words: Dielectric Response, Ferroelectrics, Solid-State Reaction, X- Ray Diffraction.

INTRODUCTION

Since the discovery of barium titanate ($BaTiO_3$) in early 1940s, this material has been used for a wide range of scientific and industrial applications such as capacitors, ultrasonic transducers, pyroelectric infrared sensors, positive temperature coefficient (PTC) resistors[1-4] , etc. Being a lead free ferroelectric material, $BaTiO_3$ is an environmental friendly material, making it a good substitute for Pb containing compounds for various applications. It is a typical ferroelectric material with Curie temperature in the range of 120-130 ºC. It has a perovskite (ABO_3) tetragonal structure at room temperature[5]. Beyond T_c, in para-electric phase, its structure transforms from tetragonal to cubic. In cubic structure, it shows positive temperature coefficient of resistance (PTCR) behaviour and is used as material for PTCR devices. The perovskite structure is one of the most versatile structures for tailoring the properties of materials [6-8]. Both A and B–sites dopants are used to modify the electrical and dielectric properties of $BaTiO_3$. A lot of works have been reported on A- site doping [9-11]. It is well established that dielectric properties of $BaTiO_3$ ceramics depend not only on the nature and amount of dopants, but also on the different processing factors[12]. Not much work, however, have been reported on B- site doping and there is hardly any extensive report on the tungsten doping in barium titanate. Tungsten has been found to be effective in enhancing dielectric properties of other ferroelectric materials[13]. In the present work, structural, dielectric and ferroelectric properties of tungsten substituted barium titanate ferroelectric ceramics have been investigated and is reported here.

EXPERIMENTAL

Samples of compositions Ba $(Ti_{1-x}W_x)$ O_3; x = 0.0 and 0.15, were prepared using solid-state reaction method taking $BaCO_3$, TiO_2 and WO_3 (all from Aldrich of 99.9% purity) in stoichiometric proportions. The powders were thoroughly mixed, ground and passed through sieve of appropriate size. Mixtures were calcined at 1150 ºC for 2h in air. The calcined specimens were mixed with appropriate quantity of polyvinyl alcohol and molded into disc shape pellets by applying a pressure of 300MPa. Pellets were sintered at 1200 ºC and 1300 ºC for 2h in air. X-ray diffractograms of all the calcined and sintered samples were recorded on a Philips X-ray diffractometer using CuK_α radiations in the range $10° \leq 2\theta \leq 70°$ at a scanning rate of 0.02°/s. The sintered pellets were polished to a thickness of 1mm, coated with silver paste on both sides for the use as electrodes and finally cured at 300 ºC for 15 min. The dielectric parameters were measured from 100 Hz to 1 MHz on an Agilent 4284 LCR meter at oscillation amplitude of 1 volt. P-E hysteresis measurements were done from room temperature to Curie temperature using an automatic P-E loop tracer based on Sawyer – Tower circuit.

RESULTS AND DISCUSSIONS

Fig.1 shows the observed X-ray diffractograms of the studied samples. It is observed that single phase perovskite structure is formed in all the samples. Lattice parameters of the sample were calculated from the observed d-values in the X- ray diffractograms and refined using least square refinement method by a computer programe package – PowderX [14]. In the doped sample, some additional peaks are formed which are possibly due to unreacted tungsten oxide.

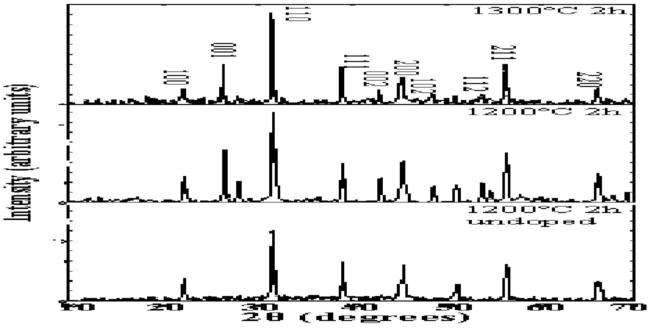

Fig. 1 XRD pattern of the studied sample

On the basis of ionic radii and co-ordination number [15], tungsten is expected to substitute titanium (B) sites (Table 1). It is observed that the lattice parameters and unit cell volume decrease on tungsten substitution (Table 1). The decreased cell volume and lattice parameters implies that the substituted W ion exists in a valence of +6, as the size of W^{6+} is smaller than Ti^{4+}.

A small variation in the position and intensity of the peaks is also observed which can be understood in terms the change in lattice parameters. On substitution of tungsten it is found that the sample is mainly composed of tetragonal phase due to splitting of (002) and (200), (102) and (201), and (112) and (211) occurring at 2θ = 43.97° and 44.83 °, 49.69 and 50.33 and 54.95 and 55.45, respectively[16].

TABLE-1

LATTICE PARAMETERS, IONIC RADII, VOLUME, DIFFUSITIVITY AND POLARIZATION VALUE

Temp.	a(A°)	c(A°)	c/a	Ionic radii (A°)	Volume $(A°)^3$	Diffusivity	$2P_r$ ($\mu C/cm^2$)
1200°C 2h Tungsten free	3.999	4.038	1.009	Ti^{4+}= 0.68	64.57	1.18	4.00
1200°C 2h	3.996	4.031	1.008	W^{6+}= 0.60	64.36	1.65	3.24
1300°C 2h	3.986	4.012	1.005	W^{6+}= 0.60	63.74	1.74	8.41

Fig.2 shows the variation of dielectric constant with temperature of the studied samples, measured at different frequencies. It is observed that on tungsten substution, T_c decreases from 115 ºC (for x = 0.0) to 85 ºC (for x = 0.15). The decrease in Curie temperature can be understood as follows.With tungsten substitution there is a reduction in Curie temperature because the bond strength between W-O is weaker as compared to Ti –O bond[17]. This decrease in bond energy leads to weaker distortion of the octahedron, which also decreases c/a ratio (also observed in Table1), resulting in the decrease of Curie temperature. It is observed that the dielectric constant of the samples show a decrease as frequency is increased from 100 Hz to 100 kHz. The dielectric constant (ε) of a material has four polarization contributions: electronic polarization (ε_e); ionic polarization (ε_i); dipolar polarization (ε_d) and space charge polarization (ε_s)[18]. Response frequencies for electronic and ionic polarization are ~ 10^{16} and 10^{13} Hz respectively; and at frequencies above 100 kHz, contribution from space charge polarization is not expected[18]. This saturation of space-charge polarization results in low dielectric constant values at higher frequencies. As frequency is increased, dielectric constant is observed to decrease in all the samples, which is a normal behavior of these materials[19] and at a frequency of 100 kHz, contribution from space charge polarization is likely to be dominant[20]. The decrease in the dielectric constant is rapid at lower frequencies and become slower at higher frequencies. At the higher frequencies the dipoles can not follow the applied ac electric field resulting in the decrease of dielectric constant at higher frequencies. The high values of dielectric constant at low frequencies can thus be attributed to the presence of such space charges in the samples.

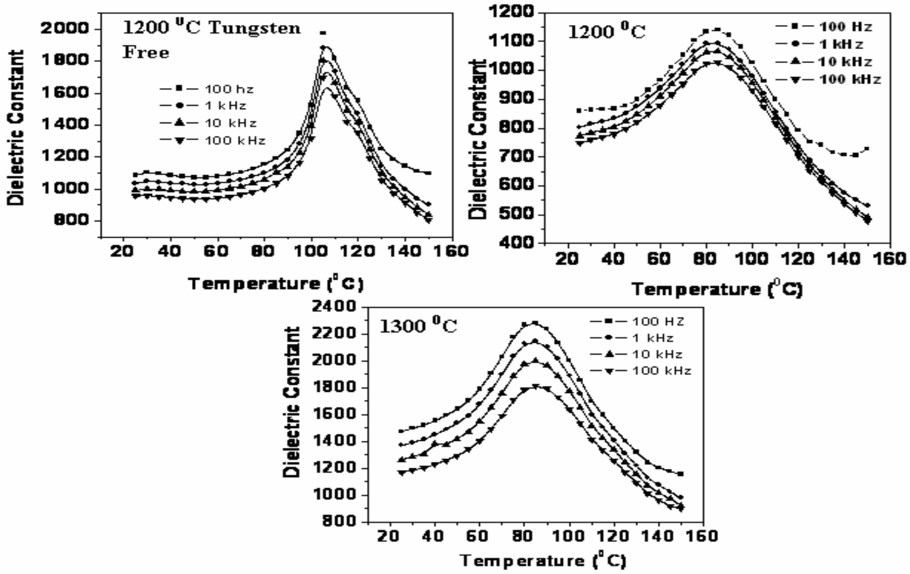

Fig. 2 Dielectric constant vs. temperature at different frequency (a) undoped sample (b) 1200 ^{0}C 2h (c) 1300 ^{0}C 2h

It is also observed that on increasing sintering temperature the dielectric constant increases. The observed maximum dielectric constant (ε_{max}) of all the studied samples is given in Table1. The increase in dielectric constant on sintering temperature can be understood as follows. It is known that in barium titanate oxygen vacancies are major structural defects [21-23]. These vacancies are generated due to the loss of oxygen during sintering at high temperature in accordance with the following relation [24]

$$O_o \rightarrow \frac{1}{2}O_2 + \mathrm{V_o^{\bullet\bullet}} + 2e$$

The above equation is in accordance with KrÖger – Vink notation of defects [25]. These vacancies act as singly ionized ion at room temperature [26]. These defects act as space charge (in the form of oxygen vacancies) in the specimen[27]. In the sample, sintered at higher temperature, larger numbers of oxygen vacancies are created. The increase in dielectric constant value is known to be related to the oxygen ions or oxygen vacancies created during sintering[28]. This is the possible cause for the increase in dielectric constant in the material.

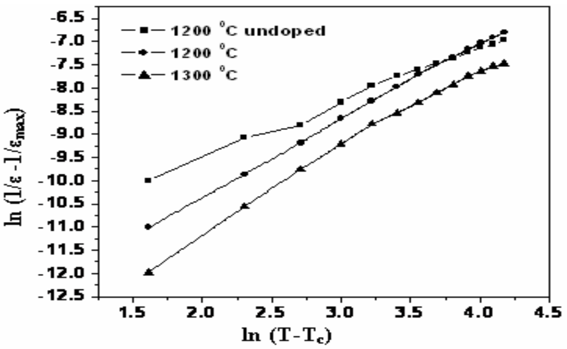

Fig. 3 Variation of ln (1/ ε – 1/ ε_{max}) as a function of ln (T- T_c).

Fig. 3 shows the variation of ln (1/ ε – 1/ ε_{max}) as a function of ln (T- T_c). Diffusivity in the sample can be calculated using the expression[29]

$$\ln (1/\varepsilon - 1/\varepsilon_{max}) = \gamma \ln (T - T_c) + \text{constant} \quad (1)$$

Where ε_{max} is the maximum dielectric constant, γ is the diffusivity or disorderness of ferroelectric to paraelectric phase transition and its value lies between 1 and 2. When γ = 1, the material follows the ideal Curie- Weiss law as in the case of normal ferroelectric while when γ = 2 the material corresponds to a complete diffuse phase transition (DPT)[30]. The calculated values of diffusivity are given in Table 1. The value of diffusivity increase with increasing sintering temperature indicating increased disordness in the system. This could be due to the increased defects (here oxygen vacancy) induced disordness[31].

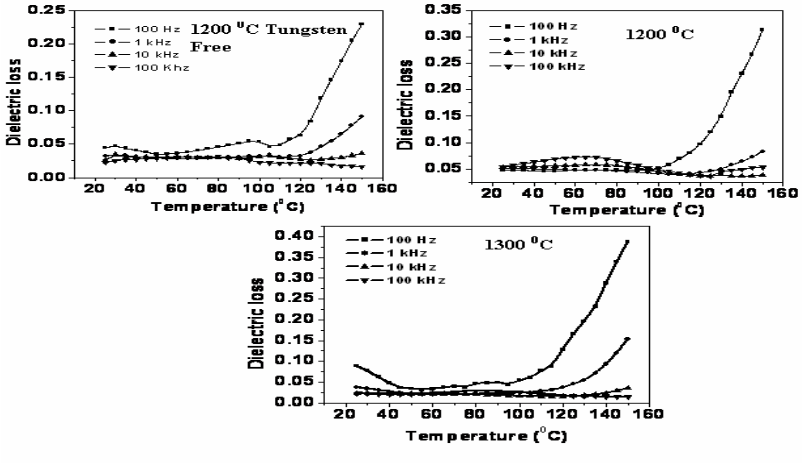

Fig. 4 Dielectric loss vs. temperature at different frequency (a) undoped sample (b) 1200 °C 2h (c) 1300 °C 2h

Fig. 4 shows the variation of dielectric loss with temperature at different frequencies. It shows negligible change upto around 100 °C, largely independent of temperature, thereafter, it increases sharply. The loss is observed to be higher at lower frequency. This can be well known that as the frequency is increased more and more dipoles are unable to follow the oscillating field resulting in the reduction in loss with increasing frequency. Further, the dielectric loss observed to increase on tungsten substitution, which is possibly due to the generation of space charges in the form oxygen vacancies, as discussed earlier. These space charges are dominant at lower frequencies and higher temperatures[32].

Fig. 5 shows the P-E loops of the studied samples at different temperatures. Well- defined hysteresis loops are formed. It is observed that $2P_r$ value increases with increasing sintering temperature. It is also observed on with increasing temperature from room temperature to Curie temperature; polarization decreases obtained at Curie temperature which indicating that the samples become paraelectric at Curie temperature and no loop is formed.

It is known that ferroelectric properties are affected by the composition, microstructure and lattice defects like oxygen vacancies in the structure of materials [33, 34-35]. In soft ferroelectrics, with higher- valent substituents, the defects are cation vacancies. Higher valent substituents and associated cation vacancies tend to form dipolar defects and random field around these dipolar defects lowers the activation barrier required for nucleation of new domains, leading to lower E_c[36, 37].Also it has been reported that cation vacancies generated by donor doping make domain motion easier and enhance the ferroelectric properties[38].

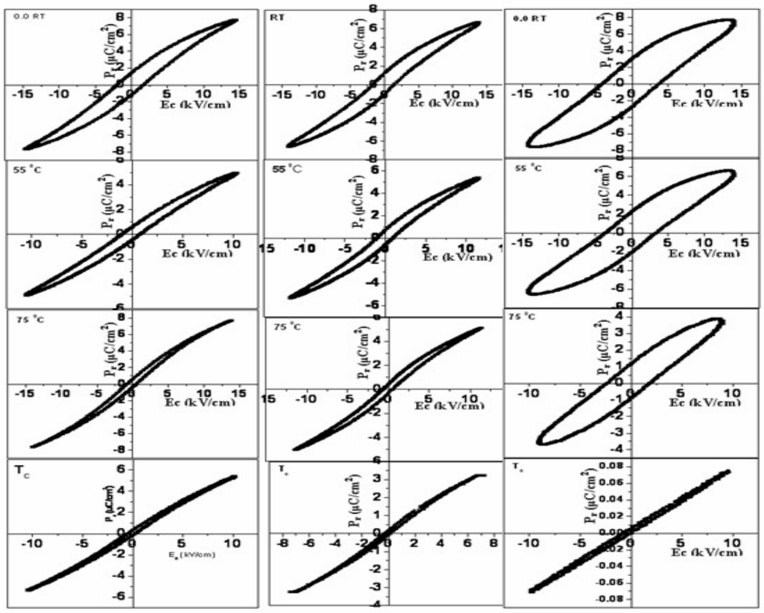

Fig. 5 P-E Hysteresis loop of (a) undoped sample (b) 1200 ºC 2h (c) 1300 ºC 2h

In the doped samples, the associated cation vacancies formation due to the substitution of Ti^{4+} by W^{6+} suppresses the concentration of oxygen vacancies. A reduction in the number of oxygen vacancies reduces the pinning effect on the domain walls, leading to enhanced remnant polarization[39].

Conclusion

X-ray diffractograms of the samples reveal the formation of single phase layered perovskite structure. The transition from ferro to para-electric becomes broader on increasing the sintering temperature as well as on substitution of tungsten indicating diffusivity in the system. Dielectric constant and loss decreases on increasing frequency. Tungsten substitution leads to higher remnant polarization ($2P_r$) values. The P-E loops become thinner as the measurement temperature approaches the Curie temperature.

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