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Structural, electrical and dielectric properties of $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ pyrochlore ceramics

A.F. Qasrawi [a,b,*], A. Mergen [c]

[a] *Group of Physics, Faculty of Engineering, Atilim University, 06836 Ankara, Turkey*
[b] *Department of Physics, Arab-American University, Jenin, West Bank, Palestine*
[c] *Metallurgical and Materials Engineering Department, Marmara University, 34722 Istanbul, Turkey*

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Abstract

The micro-structural, compositional, temperature dependent dielectric and electrical properties of the $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ solid solution has been investigated. The increasing Ta content from 0.2 to 1.5 caused; single phase formation, a pronounced grain size reduction from ~7.0 to 2.5 μm, sharp decrease in the dielectric constant from 198 to 88 and an increase in the electrical conductivity from 3.16×10^{-10} to 5.0×10^{-9} $(\Omega\ \mathrm{cm})^{-1}$, respectively. The temperature dependent dielectric constant which is found to be frequency invariant in the frequency range of (0.0–2.0 MHz) exhibited a sharp change in the temperature coefficient of dielectric constant at a (doping independent) critical temperature of 395 K. The analysis of the measured data reflects a promising future for this type of pyrochlore to be used in high voltage passive device applications.

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Keywords: A. Mixing; B. Composites; B. X-ray methods; C. Electrical properties; Dielectric

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1. Introduction

Due to their high dielectric constant and low sintering temperatures, bismuth, zinc and niobium (BZN) based ceramics have been studied extensively since 1970s. They belong to the Class-I dielectric group. The most important compound form in the bismuth, zinc and niobium system is the $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ (BZN) cubic pyrochlore. BZN pyrochlore has a low sintering temperature below 1000 °C, high relative dielectric permittivity, low dielectric loss and temperature stability [1,2]. Due to its remarkable properties, BZN pyrochlore is a promising material for microelectronic industry as multilayer capacitors and as a resonator for microwave communications.

Pyrochlore compounds with general formula $A_2B_2X_6Z$ where A is trivalent or bivalent cations, B is correspondingly tetravalent or pentavalent cations and X and Y are anions have various application areas due to their physical properties. In the pyrochlore structure, A and B cations have different coordination that the A cations are located within the distorted cube and the B cations are distorted octahedra. The A cations contain two short bonds to the Z anions and six longer bonds to the X anions. However, the B cations are equidistant from the central cations. The BX_6 groups share corners to form a three dimensional B_2X_6 network with hexagonal holes along the 1 1 1 direction. Although the A_2X chains occupy these holes, they only weakly interact with more rigid B_2X_6 network. Therefore, cation and/or anion vacancies in the A_2X network do not significantly reduce the stability of the lattice [3]. Pyrochlore compounds can accommodate various cations in the A- and B-sites due to their large stability field which impart various properties to the pyrochlores. If it is assumed that the Zn cation in the $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore is distributed evenly through A- and B-sites, the chemical formula of BZN pyrochlore can then be stated as $(Bi_{1.5}Zn_{0.46})(Zn_{0.46}Nb_{1.5})O_{6.92}$ which is an A-, B-sites and oxygen deficient pyrochlore.

To alter their properties, various types of ions were doped into the BZN ceramics. For example, Huiling and Xi [4] studied

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* Corresponding author at: Group of Physics, Faculty of Engineering, Atilim University, 06836 Ankara, Turkey. Tel.: +90 312 5868329; fax: +90 312 5868091.

E-mail addresses: atef_qasrawi@atilim.edu.tr, aqasrawi@aauj.edu (A.F. Qasrawi).

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the dielectric relaxation in Ti doped $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ pyrochlore ceramic. Ti incorporation decreased the dielectric relaxation temperature, increased the permittivity of the ceramics. In addition, 2 mol% V was doped into the $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ pyrochlore as sintering aid. It decreased the sintering temperature of BZN pyrochlore to 850 °C [5]. Moreover, Sr incorporation into the A-site of $Bi_{1.5}Zn_{1.0}Nb_{1.5}O_7$ pyrochlore instead of Zn significantly affected the dielectric properties [6]. Sr substitution increased the temperature coefficient considerably without significant decrease of dielectric constant. Furthermore, Mn and W substituted BZN pyrochlores were suggested as potential candidates for multi-player devices.

In our previous work, we have studied the optical properties of the pure BZN ceramics. We have found that the BZN pyrochlore exhibits an indirect transitions band gap of 3.30 eV [7]. The room temperature refractive index was also determined and analyzed to determine the dispersion and oscillator energies, static and lattice dielectric constants and static refractive index of the pure BZN pyrochlore. Here in this work we will concentrate on the tantalum doping effects on the structural, compositional, electrical and dielectric properties of the bismuth, zinc and niobate system.

2. Experimental

Ta doped BZN ceramic powders having the composition $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ where $x = 0.0$–1.5 were prepared by the conventional high temperature solid state reaction technique. Starting materials of Bi_2O_3 (99.99%, Aldrich), Nb_2O_5 (99.5%, Merck), ZnO (99.5%, Aldrich) and Ta_2O_5 (99%, Alfa Aesar) were mixed by ball milling for 15 h in ethanol using zirconia balls. After drying, the powders were calcined at 800 °C for 4 h and they were milled in an agate mortar. The powders were pressed into disks with 1–2 mm thickness and 10 mm diameter and they were sintered between 1025 and 1050 °C for 4 h in air in a tightly closed alumina crucible to prevent evaporation losses. X-ray diffraction analysis was performed using an X-ray diffractometer (Rigaku, Cu K_α radiation, 1°/min) using powdered samples and the unit cell parameters were computed by the least square method. The densities of the samples were measured by Archimedes method. The scanning electron microscope SEM (JEOL 5910LV) was used to examine the microstructures of the sintered ceramics on fracture surfaces and surface scanning electron microscopy images were also used to determine the grain size in the samples. For this purpose, three SEM micrographs were taken and the grain sizes were measured by line intercept method. The dielectric measurements of Ta doped BZN ceramics were performed at frequencies from 1 kHz to 2 MHz on silver-plated discs using a high precision LCR meter (HP 4284A). The temperature dependence of the dielectric properties was measured using an automated system consisting of a PC, a HP 4284 LCR meter and a temperature chamber. The electrical conductivity was measured by a high temperature home made cryostat connected to A Keithely 485 Pico-ammeter and Phywe high voltage source.

3. Results and discussion

3.1. X-ray diffraction

Because the ionic radius of Tantalum (Ta) element is the same as the radius of Nb ion (0.69 Å), Ta was doped into the B-site of BZN pyrochlore in place of Nb. Ta content at all ratios between $x = 0.0$ and 1.5 using the formula of $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ resulted in a single phase formation. Consistent with the published literature X-ray powder diffraction data [8,9] for $Bi_{1.5}Zn_{0.92}Nb_{1.5}O_{6.92}$ pyrochlore ceramics, the reflected X-ray patterns, presented in Fig. 1, did not show any secondary phase in the structure of the BZN, indicating that replacement of Nb by Ta forms a complete substitutional solid solution.

To observe the effect of Ta content on the structural properties of BZN pyrochlore, the scanning electron microscopy technique (SEM) was also used. Fig. 2 shows the SEM micrographs of Ta doped BZN for $x = 0.2$ and for $x = 1.5$. As suggested by XRD, SEM examination also gives single phase structure. However, the replacement of Nb with Ta has a significant effect on the BZN grain size. For the illustrative samples shown in Fig. 2(a)–(h), as the Ta concentration increases from $x = 0.2$ (Fig. 2(a), (c) and (e)) to $x = 1.5$ (Fig. 2(b), (d) and (f)), the grain size is considerably reduced from ∼1.0–7.0 μm to ∼0.5–2.5 μm, respectively. In addition, BZN sample containing high amount of Ta ($x = 1.5$) exhibited high amount of porosity. Fig. 2(g) and (h) reflects the energy dispersive spectra for the samples doped with 0.2 and 1.5 Ta, respectively. The spectra show that the content of the samples is composed of Bi, Zn, Nb, Ta, and O only. No other elements were observed. This result indicates the homogeneity and purity of the prepared samples.

It must be noted that several trails of the thermal etching at the surfaces were handled. The trails included thermal etching at temperatures of 150–200 °C below the sintering temperature. However, even after 2 h of thermal etching, grain boundaries were unclearly observable. For this reason the fracture surfaces were examined.

The grain size attenuation with increasing Ta content may be attributed to the internal energy re-stabilization. Grain growth

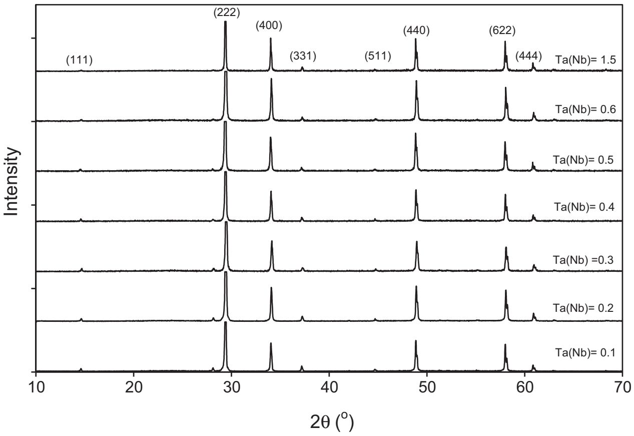

Fig. 1. XRD patterns of $x = 0.1$–0.6, and 1.5 values for $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ structure.

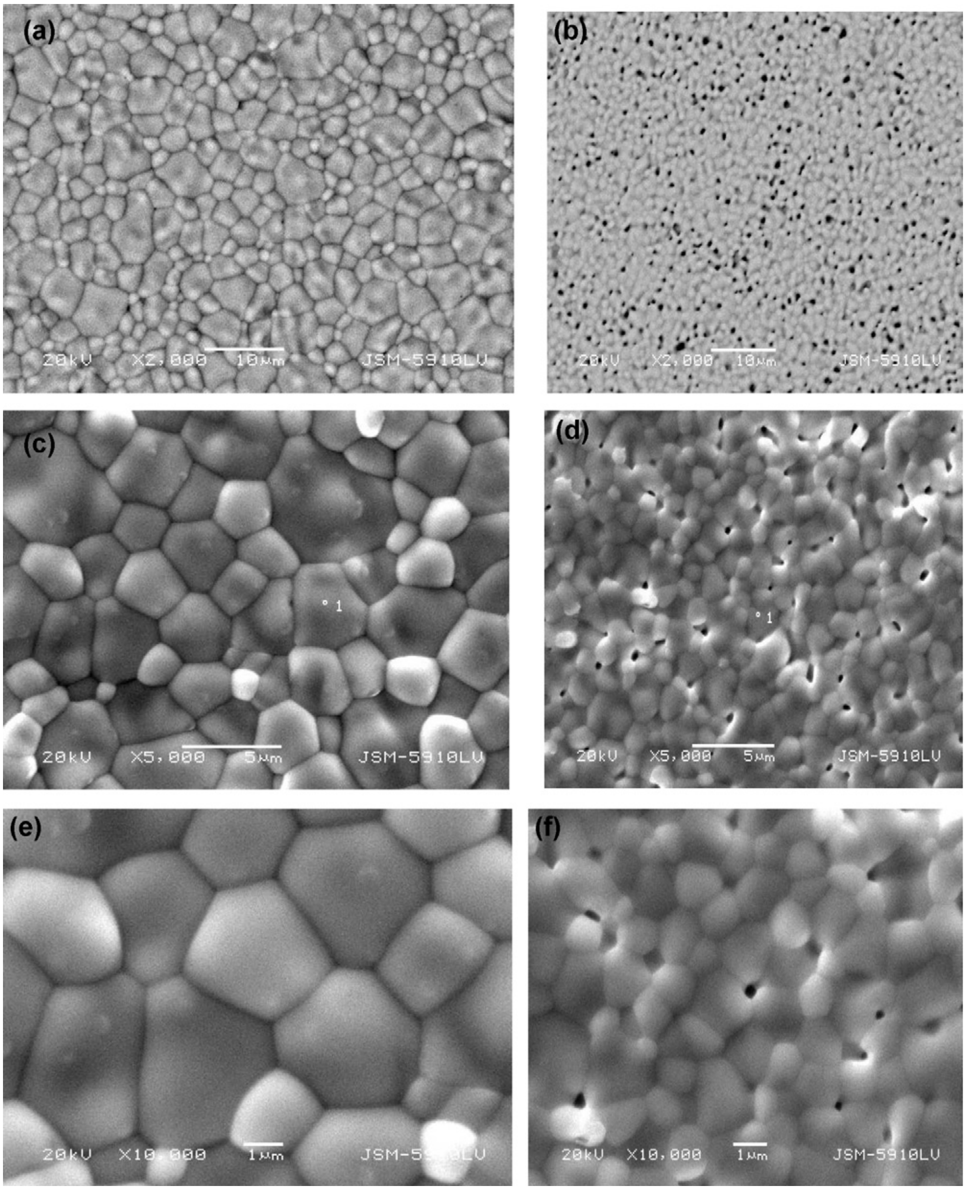

Fig. 2. SEM images of $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ pyrochlore compounds sintered at 1025 °C for 4 h (a) BSE image of $x = 0.2$ at 2×, (b) BSE image of $x = 1.5$ at 2×, (c) SEI of $x = 0.2$ at 5×, (d) SEI image of $x = 1.5$ at 5×, (e) SEI of $x = 0.2$ at 10×, (f) SEI image of $x = 1.5$ at 10×, (g) EDS of $x = 0.2$ from point 1 (pyrochlore grain) and (h) EDS of $x = 1.5$ from point 1 (pyrochlore grain).

occur when recovery and recrystallization are complete and further reduction in the internal energy can only be achieved by reducing the total area of grain boundary. In the recovery process, the deformed grains can reduce their stored energy by the removal or rearrangement of defects in their crystal structure. On the other hand, in the recrystallization process the deformed grains are replaced by a new set of unreformed grains that nucleate and grow until the original grains have been entirely consumed. In contrast to this process, increasing the Ta content may also increase the total area of the grain boundary which causes grain size reduction by dynamical re-crystallization [10,11].

It is worth notifying that for the purpose of electrical and dielectric measurements Ta doped BZN ceramics were sintered to obtain high density pellets. The sintering temperatures and the densities of Ta doped BZN ceramics are given in Table 1. The results presented in table relates to the average values of at least three identical samples to grantee high precision bulk density.

3.2. Dielectric measurements

Fig. 3(a) and (b) displays the dielectric constant variation as function of Ta content at fixed frequency (1.0 MHz) and the frequency dependence of the dielectric constant at fixed Ta content, respectively. As it is clear from Fig. 3(a), increasing the value of x from 0.2 to 0.6 decreases the relative dielectric constant from 198 to 148. The dielectric constant reaches 88 for $x = 1.5$ in which case all the Nb cations were replaced with Ta giving pyrochlore formula of $Bi_{1.5}Zn_{0.92}Ta_{1.5}O_{6.92}$. The

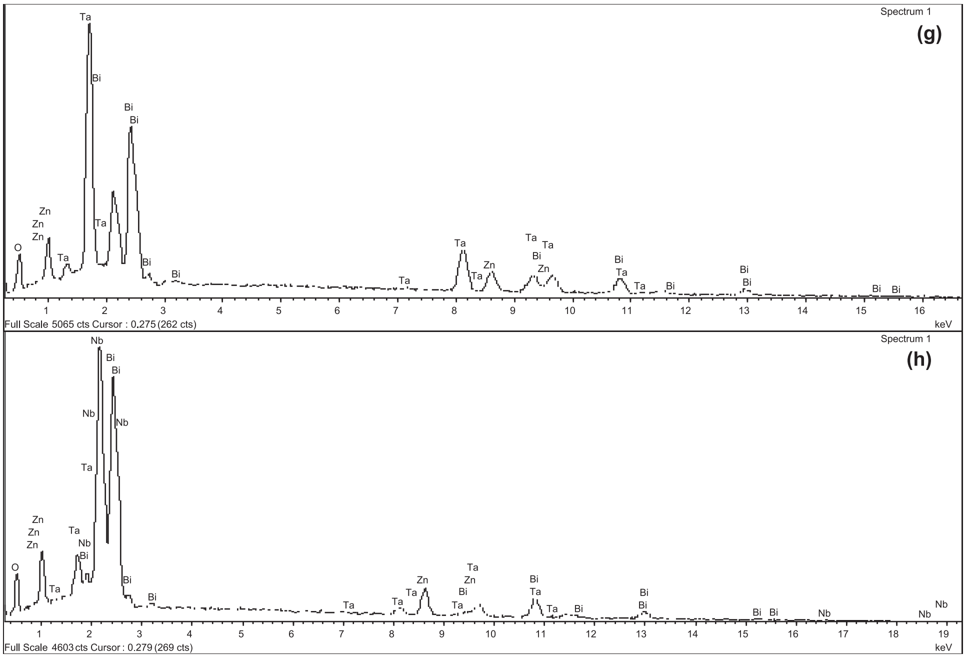

Fig. 2. (*Continued*).

Table 1
Density values and sintering temperatures of doped single phase BZN ceramics.

Substitute for	Cation	Additive proportion	Theoretical density	Bulk density	Relative density (%)	Sintering temp. (°C)
Nb	Ta	$x = 0.2$	7.273	7.08	97.4	1025
		$x = 0.4$	7.460	7.24	97.0	1025
		$x = 0.6$	7.674	7.49	97.6	1025
		$x = 1.0$	8.075	7.84	97.1	1050
		$x = 1.5$	8.575	8.35	97.4	1050

decrease of dielectric constant with increasing Ta content may be attributed to the grain size reduction (Fig. 2). The value of the dielectric constant at particular Ta content which is illustrated in Fig. 3(b) is frequency invariant.

The data presented in Fig. 4(a) and (b) illustrates the variation of $\varepsilon(\omega)$ with temperature (T) for the samples which contain 0.2 and 0.6 of tantalum, respectively. For both samples the higher the temperature the lower the $\varepsilon(\omega)$ value. The decrease in the dielectric constant with increasing temperature is systematic at each applied frequency. This observation can be easily seen from Fig. 4(c). At particular frequency and particular Ta content, the $\varepsilon(\omega) - T$ dependence is linear for temperatures less than 395 K. For temperatures greater than 395 K, the dielectric constant sharply falls with temperature indicating the increase in the pyrochlore conductivity. As may be seen from Fig. 4(c) this critical temperature ($T_c = 395$ K) does not depend on Ta content. It is the same for both samples at all frequencies. For temperatures less than T_c, the temperature coefficient of dielectric constant, α_ε, which was calculated from the relation $\alpha_\varepsilon = (\varepsilon_{T_2} - \varepsilon_{T_1})/(\varepsilon_{T_1}(T_2 - T_1))$ with T_1 and T_2 being 298 and 393 K, respectively, was found to increase from -760 in pure BZN to -509 for $x = 0.2$ and reaches -190 ppm/°C at $x = 1.5$. Although the temperature coefficient of dielectric constant is relatively high, it is still in the acceptable range of microwave ceramics (MC). Values of ~ -1100 ppm/°C are reported for the commercial MC-100 composites by the TRAK Ceramics, Inc.

In addition to the reduction of grain size observed by SEM, the decrease in the value of the dielectric constant with temperature may also be attributed to the contribution of more than one type of polarization, electronic, ionic, dipolar and space charge polarization. The nature of the variation of the dielectric constant as function of temperature and frequency determines which contribution is dominant [12]. For temperatures less than T_c, the dielectric constant is frequency independent indicating no role of applied electric field on the electronic polarization processes. In this region the decrease of dielectric constant with temperature may be mainly due to the contribution of the same type of polarization. For temperatures greater than T_c, either the type of polarization may have changed causing faster decay of dielectric constant with increasing temperature or a new structural phase may have been created. The later is less probable because the samples did not show different characteristics after re-cooling and re-heating. In other words, the values of the dielectric constant are reproducible in each characterization cycle.

The dielectric properties of Ta doped BZN was also examined by Huiling and Xi [13] they have produced $Bi_{1.5}ZnTa_{1.5}O_7$ pyrochlore by solid state reaction and reported the dielectric constant as 76 (at 1 MHz). Khaw et al. [14] also

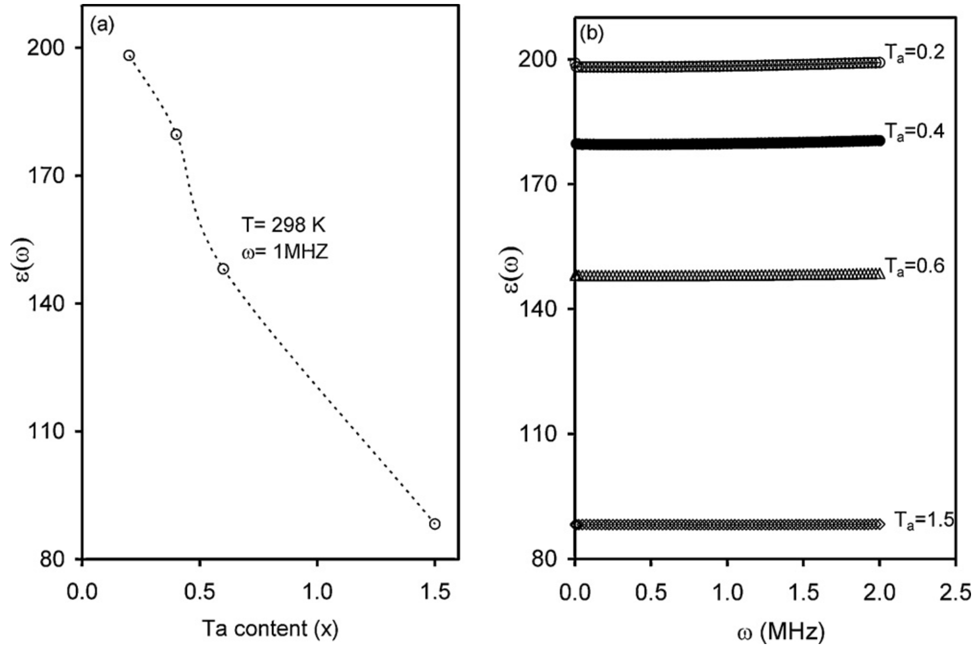

Fig. 3. (a) The doping effect on the dielectric constant of BZN. (b) The $\varepsilon(\omega) - \omega$ dependence.

studied the dielectric properties of $Bi_{1.5}ZnTa_{1.5}O_7$ pyrochlore and reported permittivity of 58 (at 1 MHz). The dielectric properties obtained in the present study were close the literature values.

3.3. Electrical conductivity measurements

Fig. 5 illustrates the dark electrical measurement results on the Ta doped pyrochlore. In general Ta doped BZN pyrochlore exhibits very low conductivity. The resistance of the samples exceeds $10^{10}\,\Omega$ at room temperature. The high resistance makes accurate data recording impossible at low electric fields. Thus data presented in figure correspond to an electric field of 1000 V/cm (an applied voltage of 150 V) between electrodes. For different contacted sample surface areas, the room temperature current–voltage characteristic (shown in Fig. 5(a)) is found to be linear over a wide range of voltage (200–1000 V) indicating; the Ohmic nature of contacts and the accurate electrical conduction at high electric field. Fig. 5(b) shows the change in electrical conductivity as function of Ta content. The change of electrical conductivity with doping is weak. The only pronounced change is observed for the sample

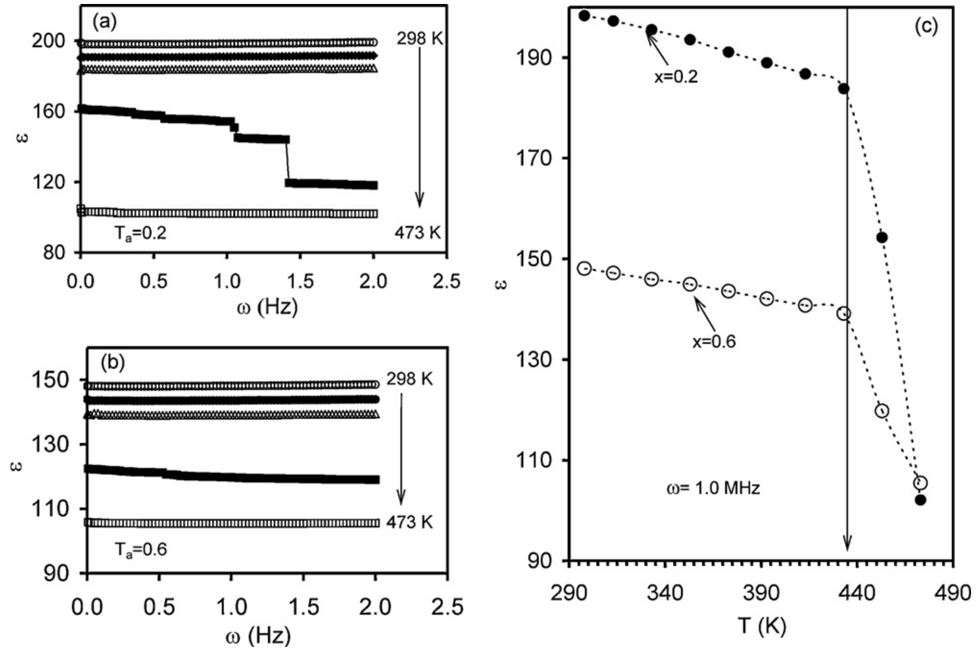

Fig. 4. The temperature dependent of $\varepsilon - \omega$ variation for (a) $x = 0.2$ and (b) $x = 0.6$. (c) The $\varepsilon - T$ dependence at 1.0 MHz.

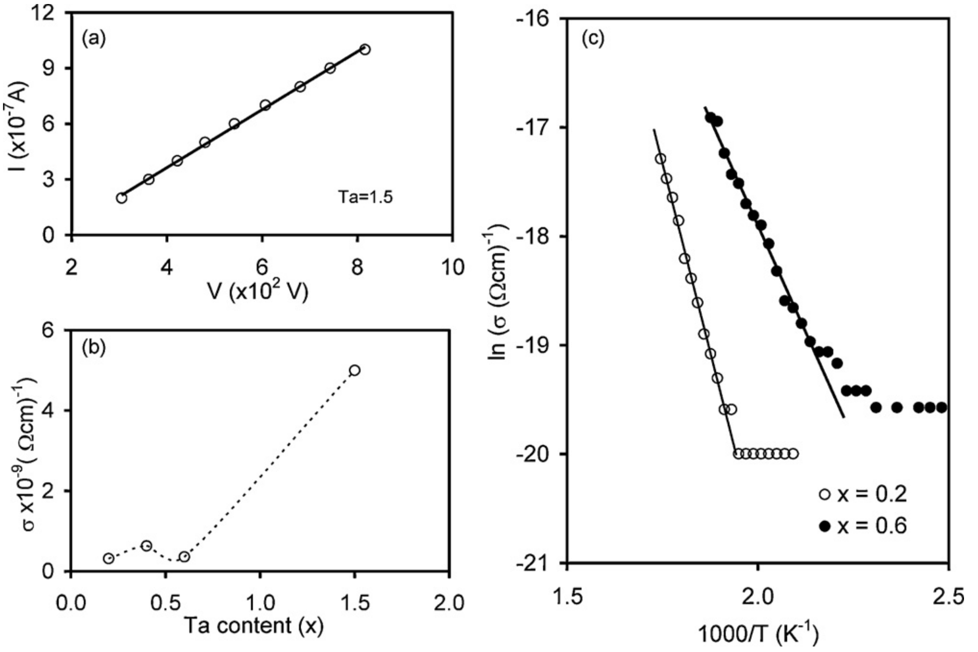

Fig. 5. (a) The *I–V* characteristics for $Bi_{1.5}Zn_{0.9}TaO_{6.92}$ at 298 K. (b) The Ta content effect on the conductivity of BZN pyrochlore. (c) The temperature dependent conductivity of Ta doped BZN.

which does not contain Nb (for $x = 1.5$). The value of the room temperature electrical conductivity increased from 3.2×10^{-10} to 5.0×10^{-9} $(\Omega\ \mathrm{cm})^{-1}$ as Ta content increased from 0.2 to 1.5. The very low electrical conduction in the BZN pyrochlore may be due to the forbidden nature of the wide band gap of BZN (3.3 eV) [7]. The increase of the electrical conductivity within replacement of Nb by Ta is probably due to the valence electrons and filling orbits of Nb and Ta which are $4d^45S^1$ and $5d^36S^2$, respectively. The $Bi_{1.5+x}ZnNb_{1.5}O_{7+1.5x}$ pyrochlores with $x = -0.1$, 0.0 and 0.1 are also reported to exhibit very low conductivity values of 1.75×10^{-16}, 10.0×10^{-16} and 1.85×10^{-16} $(\Omega\ \mathrm{cm})^{-1}$, respectively. The very low conductivities are accompanied with high dielectric constants (150) and negative dielectric temperature coefficients of −500 ppm/ °C and are attributed to the location of Nb^{5+} in the center of octahedral structure [9,15].

The temperature dependence of electrical conductivity was studied for samples doped with 0.2 and 0.6 in the temperature region of 400–530 K (stable and accurate data was possible in that region). As may be observed from Fig. 5(c), the electrical conductivity does not change with temperature for temperatures less than ~450 K. This is because the thermal energy given to the electrons in the valence band is not enough to contribute to the electrical conduction. Above 450 K, the electrical conductivity increases sharply with increasing temperature following and exponential type of growth ($\sigma \alpha \exp(-E_\sigma/kT)$). The variation of $\ln(\sigma)$ with T^{-1} are linear with slopes represented by the solid lines in Fig. 5(c). From the linear slopes, the conductivity activation energies E_σ was determined as 1.22 and 0.68 eV for the samples doped with 0.2 and 0.6 Ta, respectively. The decrease in the conductivity activation energy with increasing Ta content reflects the impurity level shift toward conduction or valence band by increasing the number of sharing electrons or holes.

4. Conclusions

In this work the tantalum doping effect on the compositional, structural, dielectric and electrical properties of the $Bi_{1.5}Zn_{0.92}Nb_{1.5-x}Ta_xO_{6.92}$ pyrochlore ceramics has been studied. The high Ta content is observed to have pronounced effect on the micro-structural, dielectric and electrical properties of the pyrochlore. Significant decrease in the crystallite size and dielectric constant accompanied with increase in the electrical conductivity is observed. This behavior indicates the tunability of the dielectric constant via Ta doping ratio. At particular Ta content, and specific ac signal, the dielectric constant decreased with increasing temperature. This temperature dependent decrement is also associated with increasing electrical conductivity.

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