

STRUCTURAL AND OPTICAL PROPERTIES OF BaO-ZnO-TiO₂ TERNARY SYSTEM

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A series of (BaO)_x-(ZnO)_{1-x}-TiO₂ (x = 0.1-0.9) ceramics are synthesized via conventional solid-state reaction method. The diffraction pattern reveals that the cubic (Zn₂Ti₃O₈ & BaTiO₃) and monoclinic (Ba₂ZnTi₅O₁₃) phases are present in the resultant compositions. The average crystallite size is found to be varying between 30- 110 nm. The optical band gap energies are evaluated using UV-Visible spectral analysis. The band gap studies established the semiconducting nature of all compositions other than x = 0.1.

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1. Introduction

Ceramic materials have potential applications various fields because of their significant electrical properties [1]. In particular, the ceramic materials with ferroelectric properties are developed and utilized for a variety of applications such as; non volatile memories, medical ultrasound imaging and actuators and data storage devices [2]. The biggest applications of ferroelectric ceramics are in the areas of dielectric ceramics for capacitor applications, especially ferroelectric thin film technology [3]. The perovskite family shows a general structure of ABO₃ [4, 5]. Many ferroelectric materials such as barium titanate (BaTiO₃), strontium titanate (SrTiO₃), lead titanate (PbTiO₃), lead zirconate titanate (PZT), lead lanthanum zirconate titanate (PLZT) etc. exhibit the perovskite structure. All these are expected to be candidate dielectric materials.

Fernandez et al. [6] reported that the careful development of microstructure and homogeneous grains is indeed helpful in improving the dielectric constant of BaTiO₃ thereby increasing the capacitance of material. Therefore, these materials can work as the candidates for multilayer capacitors. Anatolii et al. [7] synthesized ceramic compositions which are quite close to BaZn₂Ti₄O₁₁ and verified the structural, microstructural and electrical properties. As per the reported results among all the samples of BaZn_{2-x}Ti₄O_{11-x} (0 < x < 0.1) compositions, the densely sintered specimen performed high dielectric constant of ~30 and low loss tangent (tan δ) [7]. In case of BaZn₂Ti₄O₁₁ (x=0) composition, very less improvement of dielectric properties is observed. In respect of structural properties few secondary phases such as BaTi₄O₉ and Zn₂TiO₄ are noticed. Obradovic et al. [8, 9] reported that the pure BaZn₂Ti₄O₁₁ phases are formed after sintering at a temperature of 1250°C. Caballero et al. [10, 11] discussed the microstructure and electrical properties of ZnO doped barium titanate. This researcher reported that addition of ZnO (10 %) in BaTiO₃ ceramics establishes formation of fine and homogeneous grains in the microstructure. Moreover, the highest dielectric constant ~ 3000 and low loss ~ 0.01 are attributed to the same composition which can be attributed to occupation of Zn²⁺ cations in Ba²⁺ sites [10]. Roth et al. [12] used a ternary system BaO-ZnO-TiO₂ for microwave dielectric applications. This ternary system reveals the presence of four significant phases including their structures such as BaZn₂Ti₄O₁₁ (orthorhombic), Ba₄ZnTi₁₁O₂₇ (monoclinic), Ba₂ZnTi₅O₁₃ (monoclinic) and Ba_xZn_xTi_{8-x}O₁₆. The pictorial representation of all the above mentioned structures is clearly shown in reference [12]. The stability temperatures of these four phases are explained using compatibility

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triangles is illustrated. In the recent literature Naidu et al. [13, 1, 3, 4], Kumar et al. [14] and Maddaiah et al. [15, 16] investigated the effect of various elements (La, Mg, Mn, Cu, Zn & Bi) on electrical properties such as dielectric constant, loss, thermoelectric power, ac-conductivity and dc-conductivity of SrTiO₃ electro ceramic material. These researchers reported that the Cu-doped SrTiO₃ shows highest dielectric constant at room temperature (RT) [13].

To the best of author's knowledge in the literature survey, there is no detailed report on structural and band gap properties for distinct BaO compositions in the binary system of ZnO-TiO₂. Hence, an attempt has been made to elucidate the structural and optical properties of current materials.

2. Experimental procedure

In this study the starting materials are chosen as Ba (NO₃)₂ (99.6% purity, Sigma Aldrich), TiO₂ (99.4% purity, Sigma Aldrich) and ZnO (99.3% purity, Sigma Aldrich) to prepare the ferroelectric barium zinc titanate ceramics. Initially, the raw materials are weighed and mixed uniformly according to their stoichiometric ratio. The mixed powder is ball milled for approximately 12 h using ball miller (Retsch PM200). Furthermore, the uniformly grounded powder is pre-sintered at 1100°C for 12 h. The pre-sintered powder is again ground for nearly 2 h. The pellets of radius 0.59 cm and thickness 0.288 cm are prepared after applying 5 ton pressure using hydraulic press. The pellets are sintered at 1200°C for 2 h in conventional furnaces. Further, the pellets are characterized using XRD at room temperature (Bruker X-Ray Powder Diffract Meter, Cu_{Kα} = 0.15418 nm) and UV-Visible spectrophotometer (V-670 PC) for structural and optical properties respectively.

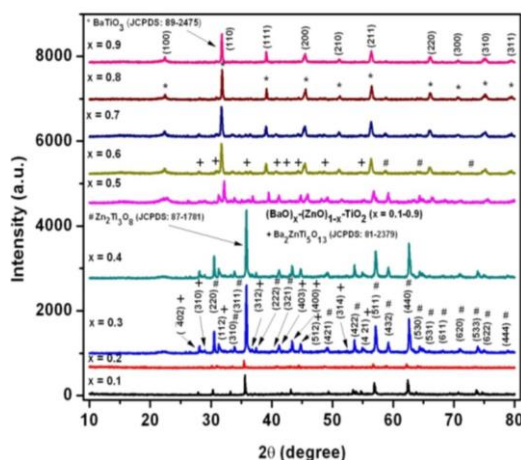
3. Results and discussions

Structural Analysis

The variation of intensity (I) as a function of two-theta (2θ) angle for the ternary system of (BaO)_x-(ZnO)_{1-x}-TiO₂ (x = 0.1-0.9) is depicted in Fig.1. It can be obviously understood from figure that with increase of 'x' in the binary system (ZnO-TiO₂) sintered at 1200°C, the intense cubic perovskite phases (indicated by #) of Zn₂Ti₃O₈ are formed up to x = 0.4 while few less intense phases corresponding to the monoclinic Ba₂ZnTi₅O₁₃ phases are appeared as the intermediate phases [12]. Thus, it confirms that the cubic phases are more dominant than the monoclinic phases. However, these monoclinic phases become decreased for x > 0.5 compositions. Beyond x = 0.5, the cubic structure is completely due to presence of BaTiO₃ phases and very few monoclinic phases of Ba₂ZnTi₅O₁₃ are also detected. The similar monoclinic phases are detected in ZnO doped BaTiO₃ compound as reported by Roth et al. [12]. The maximum intense peaks of cubic BaTiO₃ and Zn₂Ti₃O₈ phases are observed at two-theta angles 31.86° and 35.56° respectively. This establishes a new fact that the cubic to monoclinic structural transformation occurs among the compositions i.e. below x = 0.5, the resultant compound is of cubic structure pertaining more number of monoclinic phases while beyond x = 0.5, it is also of cubic structure possessing very less number of monoclinic phases. This is obviously seen in Fig.1. It is also clear from the diffraction pattern that the high barium content is dominating the total structure in the resultant compound. The reflection planes and two-theta angle positions are in consistent with the standard JCPDS data card No's: 89-2475 (cubic), 81-2379 (monoclinic) and 87-1781 (cubic) as shown in Fig.1. It is an observed fact from the literature that this kind of structural transformation can affect the distinct electrical properties [17-19].

Table.1 Data on bulk density of $(\text{BaO})_x\text{-(ZnO)}_{1-x}\text{-TiO}_2$ ($x = 0.1\text{-}0.9$) ceramics

S.No.	x	D_b (g/cm^3)
1	0.1	3.326
2	0.2	3.398
3	0.3	3.140
4	0.4	3.014
5	0.5	3.610
6	0.6	4.310
7	0.7	4.013
8	0.8	4.220
9	0.9	4.518

Fig.1. The XRD spectra of $(\text{BaO})_x\text{-(ZnO)}_{1-x}\text{-TiO}_2$ ($x = 0.1\text{-}0.9$) ceramics

In addition, the average crystallite size of all compositions is evaluated using the Scherrer formula [20]:

$$D = 0.9\lambda/\beta\cos\theta \quad (1)$$

Where λ is the wavelength of radiation used, β is the full width half maximum (FWHM) of diffraction peaks and θ is the diffraction angle. The composition dependence of crystallite size as well as the FWHM is depicted in Fig. 2. It can be seen from figure that the FWHM is increasing (from $0.150\text{-}0.297^\circ$) with increase in 'x' up to 40 % of BaO addition. For further increase of 'x' it starts decreasing (from $0.221\text{-}0.038^\circ$). On the other hand, the 'D' value is decreasing with dopant from $\sim 45\text{-}28$ nm up to $x = 0.4$ while it is showing increasing trend from $\sim 44\text{-}109$ nm. Therefore, this behaviour attributes an inversely proportional relationship between 'D' & ' β '. Similar relationship is reported in the literature [21]. The bulk density D_b ($D_b = m/\pi r^2 t$) is calculated from the mass and dimensions of the pellets [22] and listed in Table.1. The obtained results are found to be varying between $3.014\text{-}4.518$ g/cm^3 . The results reveal that D_b is almost decreasing with x value from 0.1 to 0.4. But beyond $x = 0.4$, it is increasing.

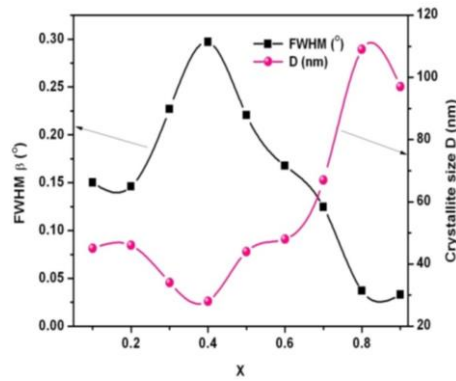


Fig.2. Composition dependence of crystallite size and FWHM

UV-Visible Spectral Analysis

The diffuse reflectance spectrum (DRS) is recorded in the range of 200-500 nm (Fig.4 (a)) for finding optical band gap energy of powder samples. The maximum absorption wavelengths are recorded as 307, 327, 340, 314, 353, 341, 338, 343 and 342 nm for $x = 0.1$ to 0.9 respectively.

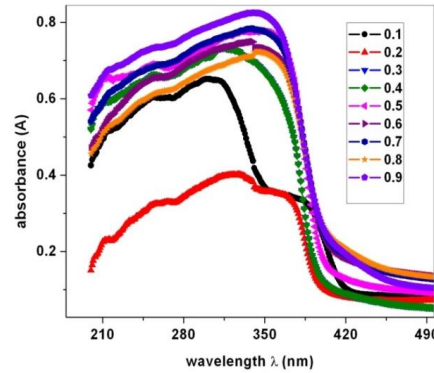


Fig.3 The absorption spectra of $(\text{BaO})_x-(\text{ZnO})_{1-x}-\text{TiO}_2$ ($x = 0.1-0.9$) ceramics

Kubelka- Munk function of reflectance $F(r)$ is used to determine band gap [23].

$$F(r) = \frac{(1-r)^2}{2r} \quad (2)$$

The absorption coefficient (α) is directly proportional to $F(r)$ and hence an equation to find band gap can be written as follows.

$$(\alpha h\nu)^n = m (h\nu - E_g) \quad (3)$$

Where m = Energy- independent constant that depends on transition probability, E_g = optical band gap energy, n = the kind of transition i.e. $n = 2$ for direct transition, $2/3$ for direct forbidden transition, $1/2$ for indirect transition, $1/3$ for indirect forbidden transition and $h\nu$ = photon energy [23]. In this study direct and indirect transitions are considered. E_{op} value is evaluated from the linear portion that is extrapolated towards X-axis for $(\alpha h\nu)^2$ versus photon energy $h\nu$ (eV) plot as α tends to zero (Fig.4 (b)). The optical band gap energies for direct transitions are 1.79, 3.65, 3.12, 3.68, 3.72, 3.15, 3.24, 3.22 & 3.21 eV and for indirect transitions are calculated as 1.55, 2.75, 3.05, 2.61, 2.60, 2.94, 2.55, 2.45 and 2.48 eV respectively. The results reveal a fact that the compositions $x = 0.2$ to 0.9 exhibit the wide band gap semiconducting nature. These values are almost equal to the optical band gap of ZnO [23].

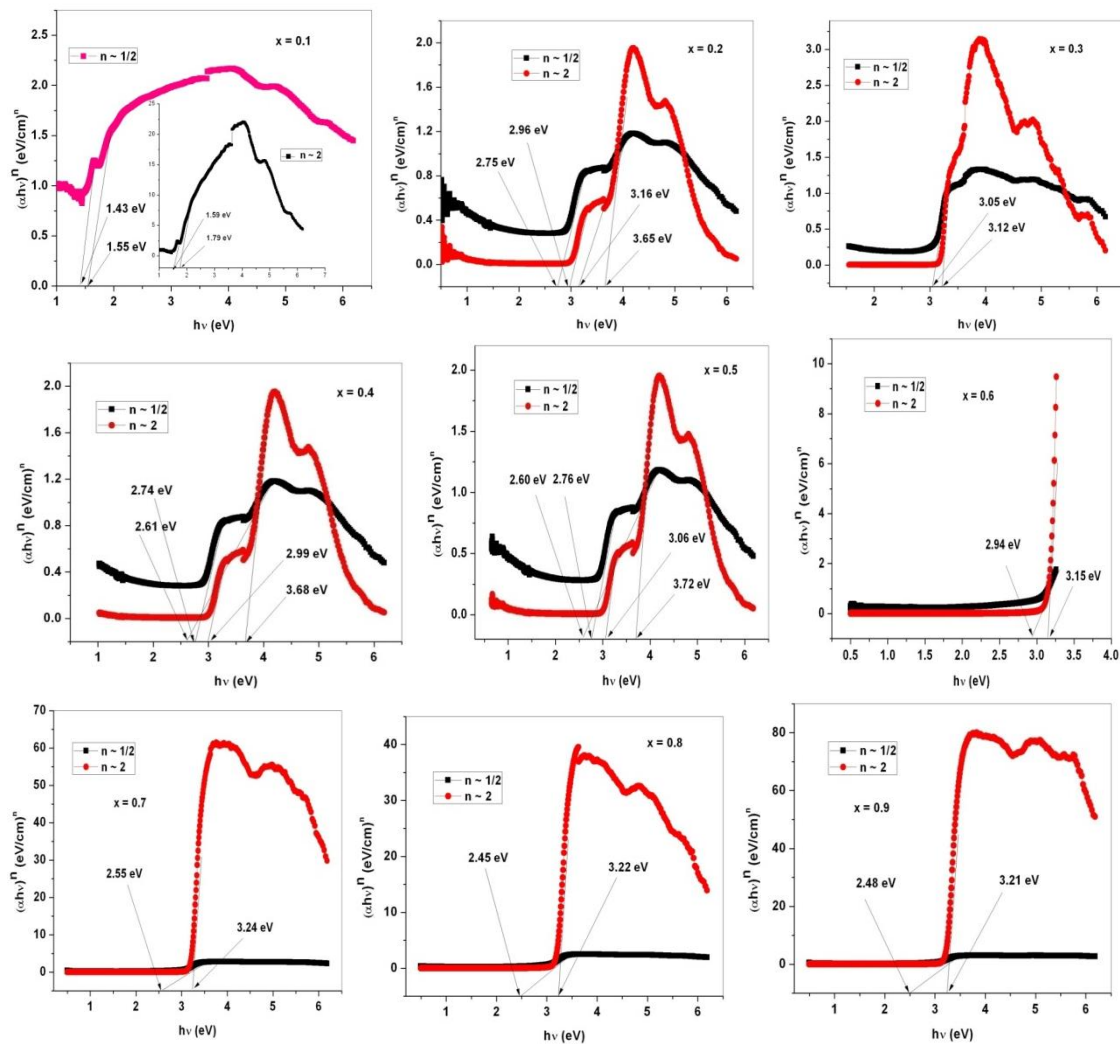


Fig.4 The $(\alpha h\nu)^2$ versus photon energy $h\nu$ (eV) plot $(\text{BaO})_x-(\text{ZnO})_{1-x}-\text{TiO}_2$ ($x = 0.1-0.9$)

4. Conclusions

The barium zinc titanate ceramic material is synthesized via conventional solid state reaction method. The cubic and monoclinic structured phases are formed in the diffraction study. A high optical band gap values for direct transitions are observed as 1.79, 3.65, 3.12, 3.68, 3.72, 3.15, 3.24, 3.22 & 3.21 eV respectively. The results reveal a fact that the compositions $x = 0.2$ to 0.9 exhibit the wide band gap semiconducting nature.

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