Investigation of optical and structural properties of scheelite-type barium tungstate ceramic

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Abstract- The manuscript presents the optical and structural behaviour of Barium tungstate synthesized by solid state reaction route. The structural characterization was studied via X-ray diffraction and microstructural analysis. The X-ray diffraction study reveals a scheelite phase with tetragonal symmetry. The optical behaviour was analysed by UV-visible spectroscopy and photoluminescence. The UV-visible shows an absorbance peak in the UV rangewith an optical band gap of 4.85 eV. A broad peak around 433 nm is obtained from the photoluminescence study.

Keywords: A. Ceramics, B. X-ray diffraction, C. scheelite. D. photoluminescence study. Barium tungstate

1. INTRODUCTION

Fabricating the phosphor-converted white light-emitting diodes (LEDs) are of much interest for present day researchers. There is a great scope for replacement of conventional light source like incandescent and fluorescent lamps with this solid state lighting technology due to their high efficiency, long lifetime, little volume, and mercury pollution-free [1,2]. The white LED can be obtained by combing a single near UV-LED chip with tricolor phosphors or combining a simple blue LED chip with yellow phosphor [3]. In this regard, various functional materials, whichpossess wide range of potential applications in various fields such as optics, electronics have synthesized and characterized. Among the functional materials m, M-WO$_4$(M=Ba, Sr and Ca)with scheelite structure have shown interesting properties[4,5].These metal tungstates have a scheelite-type tetragonal structure with space group I41/a (No. 88) and point group C64 h symmetry [6]. In the scheelite structure, alkaline earth metal ions coordinated with eight oxygen atoms and tungstate ions were connected with four oxygen atoms in the tetrahedral.These class of oxides have a wide range of technological applications as acousto-optic filters [7], solid state lasers [8,9], light emitting diodes [10], photocatalysts [11,12], phosphors [13–16], and cryogenic scintillation detectors [17]. Theself-luminescence of scheelite-type tungstates covers almost entire visible spectrum which could be decomposed in red, green, and blue components. The emission in blue region is due to the charge transfer transition withinWO$_4^{2-}$ group [18]. Among the scheelite-type tungstates, barium tungstate (BaWO4) is the heaviest and is known for itswide range of applications in lasers, radiation detection and photoluminescence. BaWO$_4$ have high refractive index, high chemical stability and high x-ray absorption coefficient which make them suitable for optical and display technologies [19, 20]. Barium tungstate crystals are prospective materials for application of Raman converters, lasers and amplifiers[21–24].In particular, barium tungstate BaWO4 (BWO) crystals have been considered as unique crystals for a wide variety of pump pulse duration that extend from nanoseconds to picoseconds[25]. In this manuscript, we report the preparation, structural and optical properties of BaWO$_4$ ceramic.

2. EXPERIMENTAL TECHNIQUES

Following the solid state reaction method ,$BaWO_4$ compoundwas prepared. The stoichiometric amount of $BaCO_3$ and WO_3 were mixed and thoroughly groundedin an agate mortar to obtain homogeneous mixture. The mixture was milled in a ball milling for 12 hrs. Then the mixed power was heated in a crucible at 1200 °C for 2 hours to ensure phase formation. The phase purity of $BaWO_4$ powder wastested by powder X-ray diffraction (XRD) (PANalyticalX'Pert Pro Powder diffractometer) using Cu Ka radiation (l = 1.5418 Å, Ni filter). The calcinied powder was pressed in to pellet of 10mm size and sintered at 1250^0C for 2 hrs. The surface morphology was examined using SEM (NOVA NANOSEM450). The pellet were crushed in to powder and UV–vis absorption spectra have been recorded for powders on PerkinElmer Lambda 750 spectrophotometer.

3. RESULT AND DISCUSSION

3.1 X-ray diffraction and microstructure:

The crystalline nature and phase purity of the obtained products are examined with XRD. Fig. 1 showsthe XRD pattern of $BaWO_4$ ceramic. All the diffraction maxima of the $BaWO_4$samples are in agreement with the standard data of scheelite phase MWO_4('Joint Committee for Power Diffractions Standards, JCPDS card NO. 43-0646').Their strongest intensity peaks diffracted from the same plane was assigned as (1 1 2). They possessscheelite structure with tetragonal crystal system which belongs to I41/a space group. Besides this, there are no additional diffractions peaks that can be attributed to impurities. This indicates that the sample is single phase. The lattice parameters were obtained using checkcell software and the lattice parameters are a = b=5.603(4) Å, c = 12.693(7) Å , V = 398.48(61) $Å^3$. The structure of $BaWO_4$ consist of the Ba cations and the tetrahedral WO_4 anions. The atom of barium is in coordination to 8 oxygen atoms situated at the polyhedral corners. The atom of tungsten is coordinated to 4 atoms of oxygen in a tetrahedral configuration and the shape of the oxygen coordination polyhedral is slightly distorted due to different angles of bonding (108.56^0 and 111.30^0) between O–W–O. The microstructure of the $BaWO_4$is presented in Fig. 2. Well define dense microstructure was observed and the sizes of the grain was in micron range.

3.2 UV-Visible spectroscopy:

Fig.3 shows the UV-vis spectra for the $BaWO_4$ceramics.The crystalline powder presents on absorption front which are well defined while the structurally disordered powders show typically a continuous smooth absorption increase as a function of the wavelength which indicates the existence of localized states within the energy band gap. The UV-vis absorption spectra of$BaWO_4$have intense absorption edges at 259 nm which lie in the UV region. The optical band gap energy (E_g) of $BaWO_4$powders was calculated following the Kubelkae-Munk method. This promotes the transformation of the measured diffuse reflectance and the extraction of E_g values with the best accuracy. In this case, for any wave length, the Kubelkae Munk [26] equation is described by equation below:

$$F(R_\infty) = \frac{(1-R_\infty)^2}{2R_\infty} = \frac{k}{S} \tag{1}$$

Where $F(R_\infty)$= Kubelkae Munk function or the diffuse reflectance of the layer relative to a non- or low-absorbing standard.$R_\infty = R_{sample}/R_{reference}$, *k*=molar absorption coefficient of the samples ($BaWO_4$ powders)

and *S*= scattering coefficient. In the parabolic band structure, the absorption coefficient and the optical band gap of semiconductor oxides can be calculated by the following equation:

$$\alpha h\nu = C_1 \left(h\nu - E_{gap} \right)^n \qquad (2)$$

Where α =linear absorption coefficient of the material, $h\nu$ =photon energy, C_1=proportionality constant, E_{gap}=optical band gap and *n*=a constant associated with the different types of electronic transitions (for direct allowed n = 1/2, for indirect allowed n = 2, for direct forbidden n = 3/2 and for indirect forbidden n = 3). In this process, the absorption of photon can give rise to an indirect electronics transition from minimum energy states in the valence band to a maximum energy state in the conduction band. This process takes place in different regions of the Brillouin zone. Accordingly, the E_g values of $BaWO_4$ powders were calculated using n = 2 in Equation (4). Finally, using the Kubelkae-Munk function given in Equation (3) and replacing of the term k with 2α, we obtain the Kubelkae-Munk modified equation as indicated in Equation (3):

$$\left[F(R_\infty)h\nu \right]^{1/2} = C_1 \left(h\nu - E_{gap} \right) \qquad (3)$$

We can determine the E_g values $BaWO_4$ powders with more accuracy from the plotting of $[F(R_\infty)h\nu]^{1/2}$ vs$h\nu$ as shown in Figure 5. The E_g value of $BaWO_4$ is found to be 4.85eV is nearly equal to the reported result. The E_g value of $BaWO_4$ ceramic is associated with an effect of structural order–disorder into the lattice due to a symmetry break between the O–W–O bonds and/or distortions on the $[WO_6]$ clusters. A reasonable explanation for the origin ofthis symmetry break can be related to the synthesis method. It is possible to conclude on this hypothesis that the high temperatures employed in the SSR method are not sufficient to avoid the structural defects (symmetry break between bonds or distortions) into the $BaWO_4$ structure.

3.3 Photoluminescence properties:

Photoluminescence spectra were used to test the ability of charge carrier trapping, transferand immigration as well as to understand the fate of photogenerated e^-/h^+particle pairs in semiconductor. The emission spectrum of $BaWO_4$ shown in Fig. 5revealed the peak at 433 nm under excitation of 350 nm. It was accepted that the emission and excitation of $BaWO_4$ ceramic mainly arise from charge-transfer transitions from the oxygen ligands to the centrally situated tungsten atom within the WO_4^{2-} complex between the last completely filled 1 orbital and the first vaccant 2e orbital [26,41].The broad band predicts that the process of emission is a typical multi phonon or multi-level process, i.e., a solid system in which the relaxation takes place by various paths, involving a number of energy states within the band gap. It is observed that $BaWO_4$ emission curves exhibit a broad luminescence in the blue wavelength range.

Fig.1
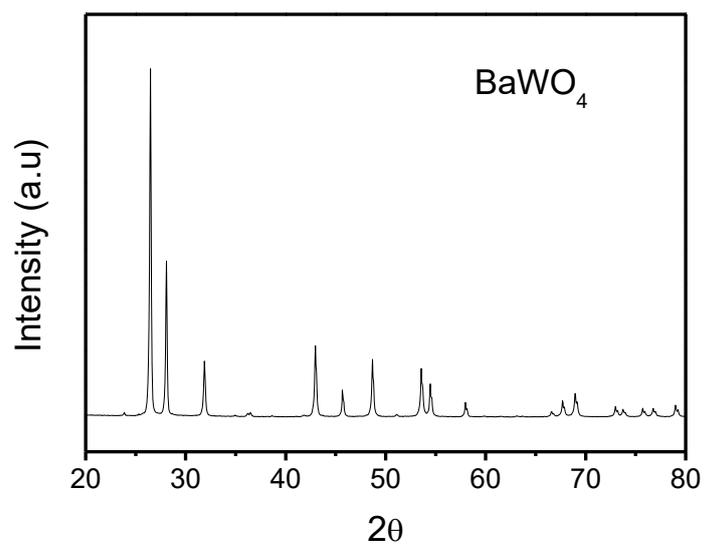

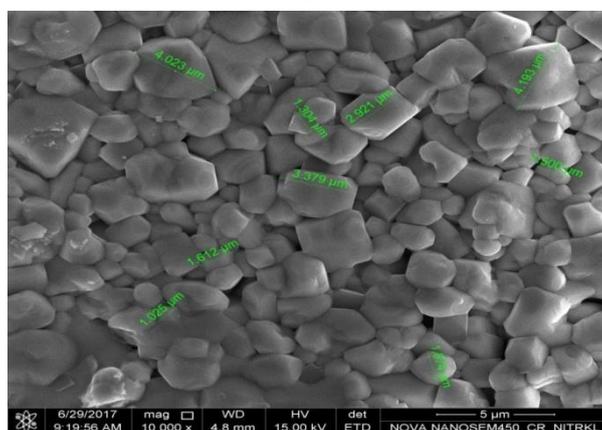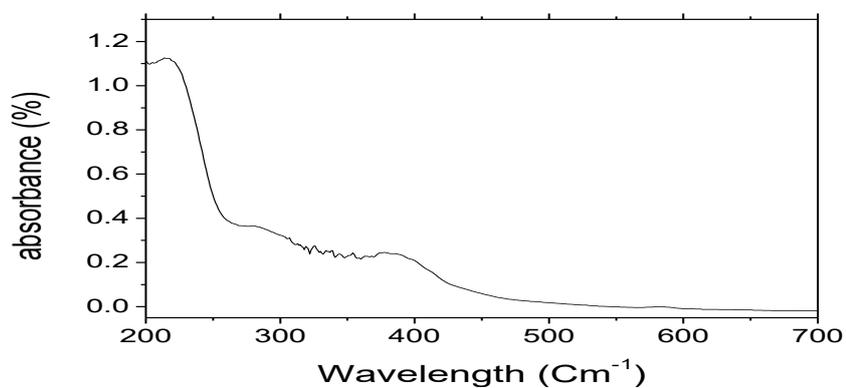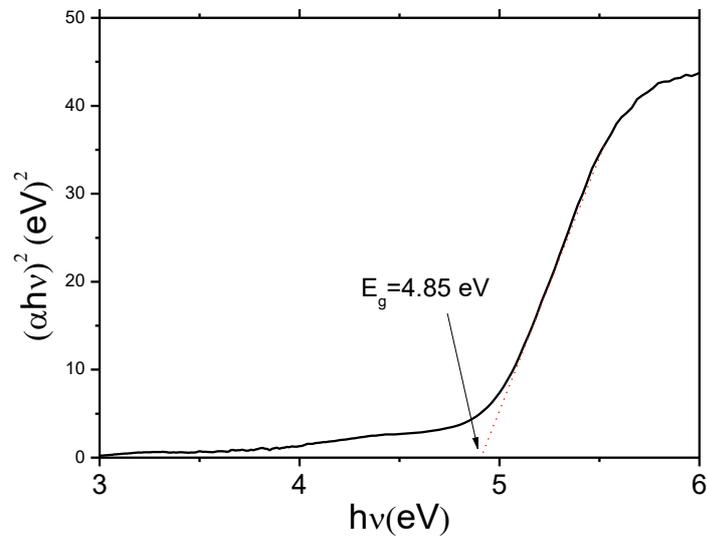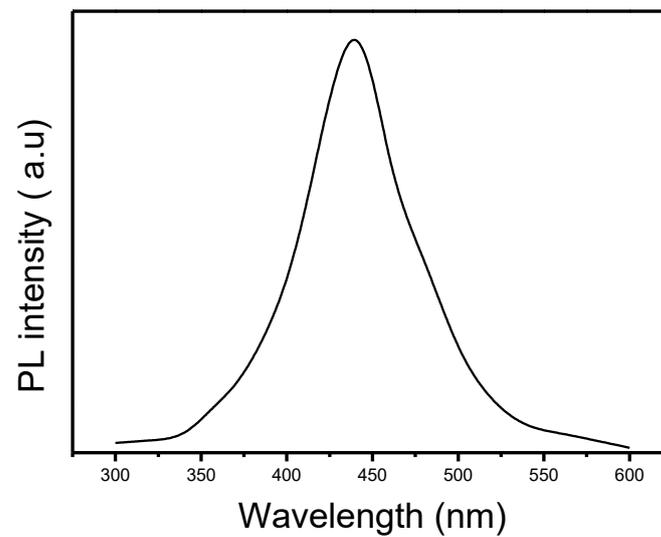
Fig.2

Fig.3

Fig.4

Fig.5

Figure caption

Figure 1: XRD pattern of BaWO$_4$ at room temperature.

Figure 2: SEM of BaWO$_4$ at room temperature.

Figure 3: UV-vis spectra for the BaWO$_4$ ceramics.

Figure 4: UV-vis spectra for the BaWO$_4$ ceramics

Figure 5: Photoluminescence spectra for the BaWO$_4$ ceramics.

4. CONCLUSION

The $BaWO_4$ ceramics wasprepared by solid state reaction route. The structural analysis shows a single phase with scheelite structure. The optical properties predicts that the absorption spectra lie in the ultra-violet region. The optical band gap was calculated using standard formula found to be 4.85 eV. The photoluminescence behaviour shows a broad spectrum around 433 nm which is may be due to the existence of multiple energy level in the system. All the above characterization shows that the $BaWO_4$ will be suitable materials for optoelectronics application.

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