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Synthesis and characterization of $ZnWO_4$ ceramic powder

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Abstract

Zinc tungstate ($ZnWO_4$) ceramic powder has been synthesized by a solid-state reaction method. A broad and intense blue emission at 472 nm has been measured from it with an excitation at 297 nm. Structural properties of this $ZnWO_4$ ceramic powder have been analyzed by carrying out the XRD, SEM, EDAX and FTIR spectral measurements. Besides these studies, dielectric properties in the frequency range of 200 Hz to 3 MHz at 300 K have also been carried out and all the obtained results are reported here.

Keywords: A. Powders: solid-state reaction; B. Spectroscopy; C. Dielectric properties

1. Introduction

It has been known that the tungstate-based inorganic materials have potential applications in various fields, such as photoluminescence, microwave devices, fiber optical communications and as scintillator materials [1–4]. These materials are considered to be novel, technically and commercially important because they posses different encouraging properties such as high chemical stability, high refractive index, high X-ray absorption coefficient and also their displaying efficiency in outputs [5–7]. As a wide direct band gap semiconductor, ZnO has recently been gaining more attention due to its extensive applications in a variety of fields [8–10]. Keeping these advantages in view, we have made an attempt here to prepare $ZnWO_4$ ceramic powder by a solid-state reaction method to characterize its spectral and dielectric properties systematically.

2. Experimental studies

Zinc tungstate ($ZnWO_4$) ceramic powder was prepared by a solid-state reaction method. Commercially available laboratory reagent chemicals of ZnO, WO_3 (in 99.9% purity) were used as starting materials. These two chemicals were weighed appropriately based on the stoichiometric composition and later on these chemical mixtures were powdered by using acetone as a wetting organic liquid in an agate mortar for 2 h. The mixture was then transferred into a porcelain crucible and later on sintered in an electrical muffle furnace at 1000 °C for about 5 h. The structure of the synthesized ceramic powder was characterized on a XRD 3003TT Seifert diffractometer with CuKα radiation (λ = 1.5406 Å) at 40 kV and 20 mA and the 2θ value was varied between 20° and 80° range. The morphology of the ceramic powder was examined on a JEOL JSM 840A Scanning Electron Microscope. The ceramic powders were gold coated using a sputter coater polaron SC7610 system. The elemental identification of the synthesized ceramic powder was obtained from the EDAX attachment of the SEM system. FTIR spectrum of the sample was recorded on a Nicolet IR-200 spectrometer using a KBr pellet technique in the range of 4000–400 cm^{-1}. Dielectric profiles of $ZnWO_4$ ceramic powder measured in the frequency range of 200 Hz to 3 MHz at 300 K on a Hioki 3532-50 LCR meter. Both the excitation and emission spectra of the sample were carried out on a Jobin Yvon Fluorolog-3 Fluorimeter with a Xe-arc lamp (450 W) as the source of excitation.

3. Results and discussion

An XRD profile of $ZnWO_4$ ceramic powder has been presented in Fig. 1 revealing that it is in *monoclinic* nature and most of the observed peaks have been indexed to the pure phase of *monoclinic wolframite* using the JCPDS Card No: 15-0774.

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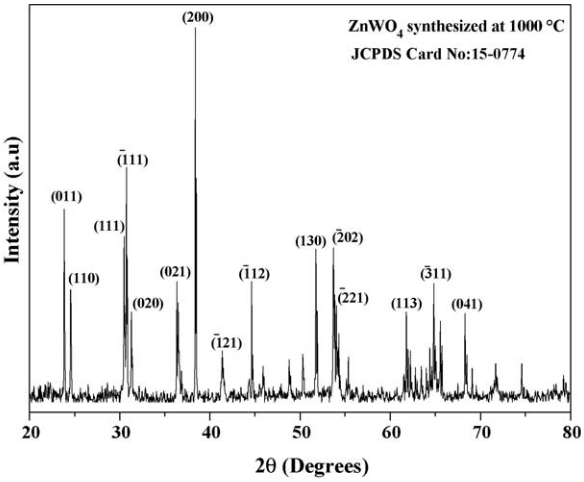

Fig. 1. XRD profile of $ZnWO_4$ ceramic powder.

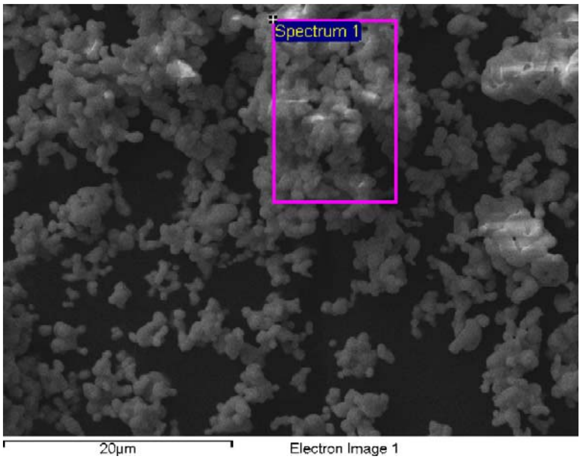

Fig. 2. SEM image of $ZnWO_4$ ceramic powder.

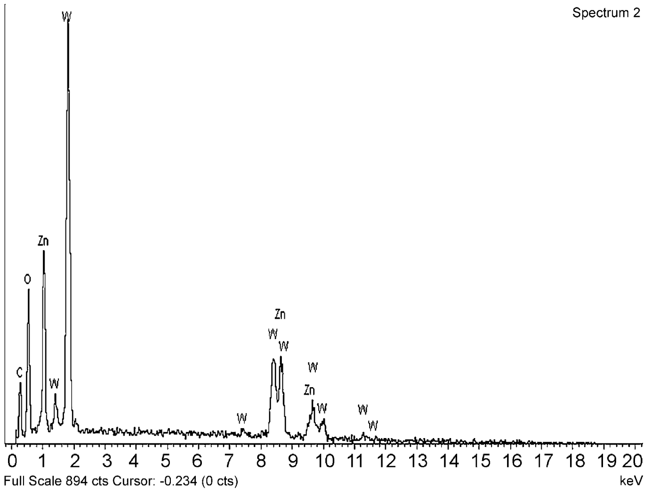

Fig. 3. EDAX profile of $ZnWO_4$ ceramic powder.

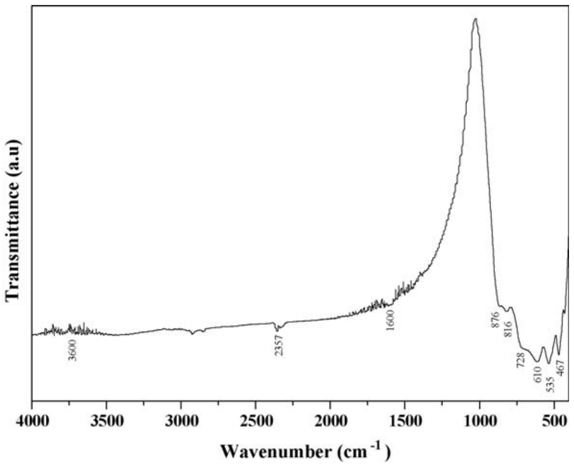

Fig. 4. FTIR spectrum of $ZnWO_4$ ceramic powder.

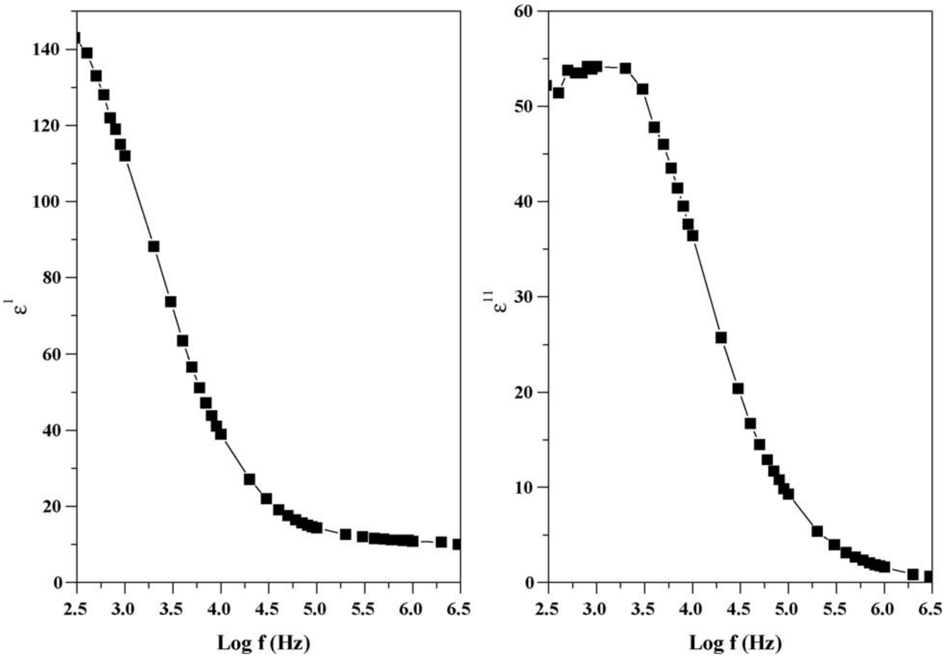

Fig. 5. Variation of dielectric constant (ε') and dielectric loss (ε'') of $ZnWO_4$ ceramic powder with respect to frequency at room temperature.

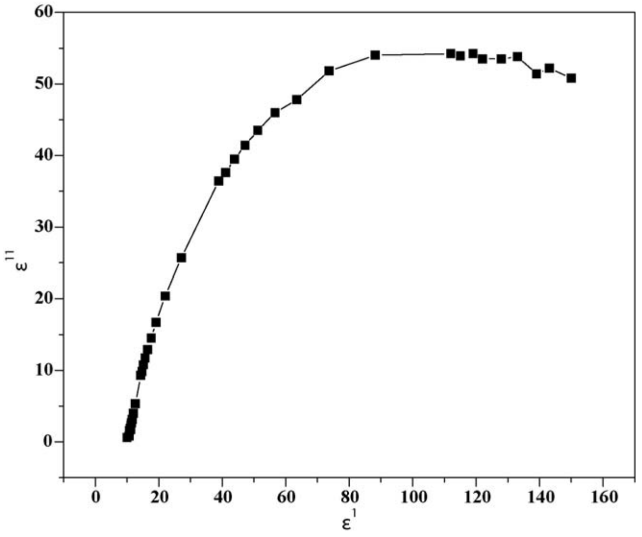

Fig. 6. Complex Argand plane plot between dielectric constant (ε') and dielectric loss (ε'') at room temperature for $ZnWO_4$ ceramic powder.

The crystallite size of the prepared ceramics was estimated from the Scherer equation, $D = 0.89\lambda/\beta\cos\theta$, where D is the average grain size, λ is the X-ray wavelength (0.15406 nm), θ and β are the diffraction angle and full width at half maximum (FWHM) of the corresponding peak [11]. Intense diffraction peaks have been selected to compute the crystallite size and it is found to be in an average size of 530 nm. The SEM micrograph of the $ZnWO_4$ ceramic powder has been shown in Fig. 2, displaying that the particles are noticed to be agglomerated and the average diameter of the grain is about 1 μm. EDAX profile of $ZnWO_4$ ceramic powder has also been shown in Fig. 3 to validate the presence of Zn, W and O elements.

The FTIR spectrum of $ZnWO_4$ ceramic powder has been given in Fig. 4, which reveals bands at 467 cm^{-1} and 535 cm^{-1} that are ascribed to the bending and stretching vibrations of Zn–O and further there are two more peaks located at 610 cm^{-1} and 728 cm^{-1} which originated from bending and stretching vibrations of W–O. There also exists a band at 816 cm^{-1} that arises from the bending and stretching vibrations of Zn–O–W [12]. A weak band at 876 cm^{-1} is assigned to the stretching mode of W–O bonds in joint WO_6 octahedral [13]. Weaker bands near 3600 cm^{-1} and 1600 cm^{-1} are due to the O–H stretching and the H–O–H bending vibrations, respectively [14]. A weak band at 2357 cm^{-1} is ascribed to the C–O vibration of CO_2 in room atmosphere [13].

Fig. 5(a) shows the variation of dielectric constant (ε') of $ZnWO_4$ ceramic powder with the change of the frequency at the room temperature. From the plots it is clear that the dielectric constant decreases with an increase in the frequency. This is due to a phenomenon of frequency dispersion [15]. The frequency of hopping between the ions could not follow the frequency of applied field and hence it lags behind, therefore the values of ε' could normally decrease at higher frequencies. Fig. 5(b) shows the variation of dielectric loss (ε'') of $ZnWO_4$ ceramic powder with the change of frequency at the room temperature and it is observed that the value of tan δ was found to increase up to a particular frequency, beyond that it decreases thus revealing the dielectric relaxation phenomena of $ZnWO_4$ ceramic powder [16]. In the dielectric materials, defects, space charge formation, lattice distortions, etc., in the boundaries could produce absorption current resulting in a loss factor (tan δ) and with high alternating frequency these could follow the field applied and then gradually come down to a

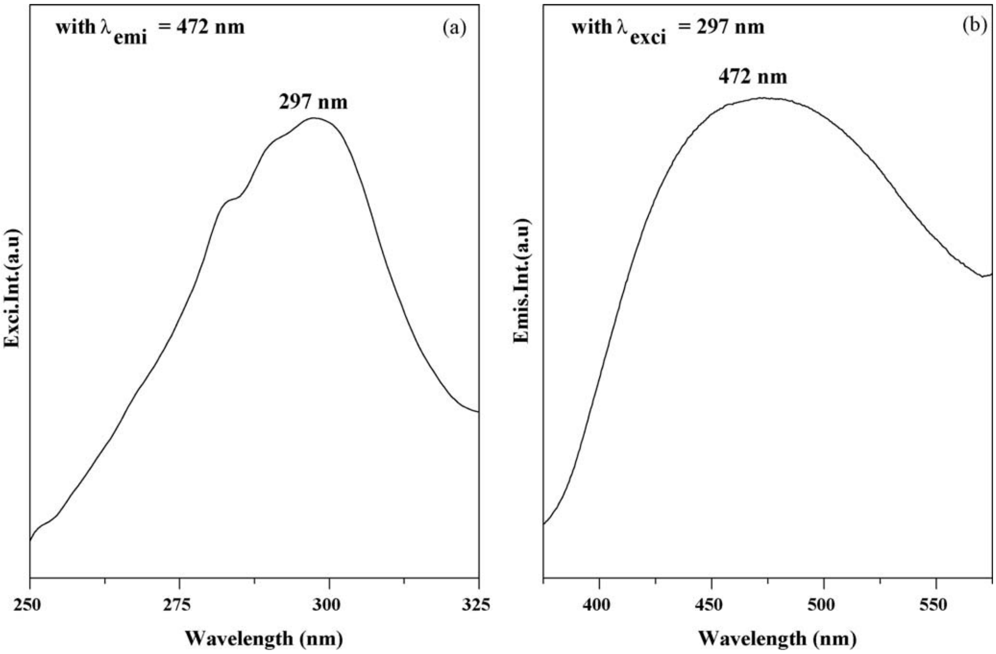

Fig. 7. (a) Excitation and (b) emission spectrum of $ZnWO_4$ ceramic powder.

low value [15]. One of the most convenient ways of checking the polydispersive nature of dielectric relaxation is through complex Argand plane plots between ε' and ε'', which are usually called Cole–Cole plots. Fig. 6 shows a room temperature representative plot. Under the pure monodispersive Debye process, semicircular plots are expected with a centre located on the ε' axis whereas, for polydispersive relaxation, these Argand plane plots are close to circular arcs with end points on the axis of real's and a centre below this axis [16]. The Cole–Cole plot confirms the polydispersive nature of dielectric relaxation of $ZnWO_4$ ceramic powder.

Fig. 7 shows both the excitation and emission spectra of $ZnWO_4$ ceramic powder that was sintered at 1000 °C. The excitation spectrum of $ZnWO_4$ ceramic powder was measured by monitoring its blue emission at 472 nm. The excitation spectrum (Fig. 7(a)) reveals a strong band due to WO_4^{2-} at 297 nm [11]. Fig. 7(b) shows the emission spectrum of $ZnWO_4$ ceramic powder in the wavelength range of 375–575 nm with 297 nm excitation showing a broad blue emission at 472 nm. This is related to the presence of WO_6 structures in the matrix, playing the role of luminescence centers and a charge-transfer transition between the O 2p orbitals and the empty d orbitals of the central W ion that could be causing this luminescence [17].

4. Conclusion

Monoclinic phase $ZnWO_4$ ceramic powder was prepared by a solid-state reaction method at 1000 °C. $ZnWO_4$ ceramic powder demonstrated a broad and intense *blue* emission (472 nm), which originates from its wolframite structure. Besides the analysis of these properties, dielectric properties of this ceramic powder were also studied to evaluate its usefulness in the progress of optoelectronic materials.

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