



Synthesis and spectroscopic characterizations of copper ions doped zinc borate nanoparticles



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ARTICLE INFO

Article history:

Received 30 December 2015

Accepted 25 January 2016

Keywords:

Co-precipitation

X-ray diffraction

Luminescence

Electron paramagnetic, resonance (EPR),

Bonding parameters

ABSTRACT

Spectral investigations of Cu²⁺-doped zinc borate nanoparticles have been reported in this paper. The as-prepared nanoparticles are characterized using powder XRD, SEM with EDS, HRTEM, optical absorption, electron paramagnetic resonance (EPR), photoluminescence (PL) and FT-IR measurements. The powder XRD patterns confirm the monoclinic crystal structure of the prepared nanoparticles. From the optical absorption spectrum, it is observed that a single broad absorption band is observed. The EPR result confirms that the Cu²⁺ ions enter distorted octahedral site symmetry at room temperature. The bonding between the metal ion and ligands is partially covalent nature. The PL spectrum exhibits emission bands in the ultraviolet and visible regions at room temperature. The CIE chromaticity coordinates indicate the prepared material shows the light in visible region. The bands observed at 475 and 549 cm⁻¹ are attributed to metal ions-oxygen and BO₄ tetrahedron in the molecular structure.

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1. Introduction

Recently, borate materials are attracted a great deal of attention owing to their structural chemistry and potential applications in luminescence and nonlinear optical properties [1]. Zinc borates (ZB) are important engineering materials, they are widely used in various industries applications [2–5], flame retardant agent in polymers [6–8], as a lubricating additive, fire retardant, corrosion inhibitor in thermal treatment [9,10], modifier of electrical and optical properties, tribological properties, wear resistance agent [11–16] and multifunctional flame retardant. In most of these applications, particle size and morphology is an important parameter.

Various methods have been developed for the preparation of zinc borate materials, solid state reaction [17–19], sol–gel reaction [20], and hydrothermal technology. These methods have disadvantages such as a complicated operating procedure and high cost. The major challenge in synthesis of inorganic nanoparticles is (i) control morphology, (ii) particle size, which is directly related to preparation method. The morphologies of precipitated ZB and their phase compositions are significantly influenced by preparation conditions like PH value, temperature, duration of experiment, type of zinc and boron salts [11,13,21], and the use of surface modifying

reagents [12–14]. The chemical synthesis method does not require special apparatus, cost effective and an eco-friendly technique.

Doping a small concentration of a paramagnetic impurity into a host lattice, it helps to detect the changes in the general characteristics of the host impurity. Copper ions are characterized by a partially-filled d shell, it can exist at least two valence states. The Cu²⁺ ion can enter easily into a number of host lattices due to its paramagnetic behavior. The optical properties are greatly influenced by doping of transition metal ions into the host lattice. To the best of our knowledge, there are fewer reports about the effect of the transition metal (TM) ion on the spectral characterizations of zinc borate materials.

In the present study, we report the synthesis of Cu²⁺ ions doped Zinc borate nanoparticles synthesized using co-precipitation method. In order to get the information about the nature of site symmetry, energy level structure, distortion in the lattice, crystal structure, bonding nature and luminescent properties, the synthesized material is undertaken by using various spectroscopic techniques and to get a comprehensive view.

2. Experimental procedure

Analar grade of zinc nitrate, Zn(NO₃)₂·6H₂O, and borax aqueous, Na₂B₄O₇·10H₂O, were used as a starting materials. 0.02 mol% Zn (NO₃)₂·6H₂O and 0.01 mol% Na₂B₄O₇·10H₂O were dissolved in deionized (DI) water separately. 0.001 mol% of Cu(NO₃)₂ solution

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was added to $\text{Zn}(\text{NO}_3)_2$ solutions with continuous stirring. The mixture was dropped into the $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ solution at 60°C under magnetic stirring. After filtering, the precipitate was washed three times with 30 mL DI water and subsequently dried in an oven at 85°C for 24 h. The obtained powder was calcined at 700°C at a rate of 10°C per min for 1 h.

2.1. Characterization

A Powder X-ray diffraction pattern (XRD) of the prepared sample was recorded using a PANalytical Xpert Pro-diffractometer with $\text{Cu-K}\alpha$ (1.54060 \AA) radiation. The sample was finely powdered and mixed with nujol (liquid paraffin) for optical recording. The optical absorption spectrum was taken using a JASCO V-670 spectrophotometer. Scanning Electron Microscopy (SEM) images were obtained from a Carl Zeiss SEM EVO with a carbon coating. The EDX spectrum was recorded on oxford Penta FET. Transmission Electron Microscope (TEM) images were recorded using TEM HITACHI H-7600 instrument. HRTEM images were taken on Tecnai G2 F 20 S-Twin TEM at an accelerating voltage of 200 kV. The FT-IR spectrum was recorded on a Thermo Nicolet 6700 using KBr pellets. The EPR spectrum of the powder sample was taken in an EPR quartz tube, and the spectrum was recorded at room temperature (RT) on a JEOL JES-TE100 ESR spectrometer operating at X-band frequencies having a 100 kHz field modulation. The photoluminescence spectrum was recorded on a Horiba Jobin-Yvon Fluorolog-3 spectrofluorimeter with Xe continuous (450 W) and pulsed (35 W) lamps as excitation sources.

3. Results and discussion

3.1. XRD, SEM and TEM studies

Fig. 1 shows the powder X-ray diffraction (PXRD) patterns of Cu^{2+} -doped zinc borate nanoparticles. All the diffraction peaks in the XRD patterns of $\text{Zn}_3(\text{BO}_3)_2$ nanoparticles show good agreement with monoclinic crystal structure of the zinc borate nanoparticles, due to presence of (400), (202), (402), (121), ($\bar{5}21$), (204), and (404) planes (JCPDS file no. 37-1486), with lattice cell parameters $a=0.2344$, $b=0.5044$ and $c=0.8385$ nm. No obvious diffraction peaks from other impurities were observed. The strong diffraction peaks demonstrate that well-crystallized product was synthesized.

The average crystalline size of the sample was determined from the XRD peak broadening using Scherrer's formula: $d=0.9\lambda/\beta \cos \theta$, where λ is the wavelength of X-ray radiation (1.5406 \AA), β is the full

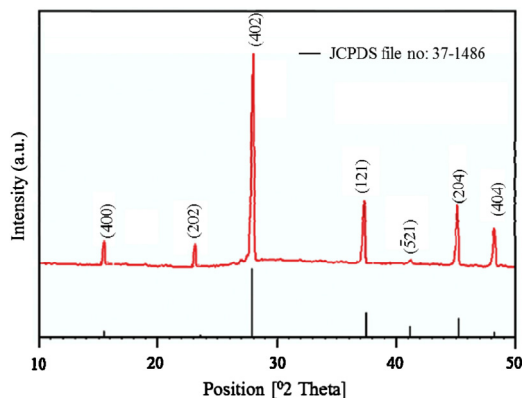


Fig. 1. Powder X-ray diffraction pattern of Cu^{2+} -doped zinc borate nanoparticles.

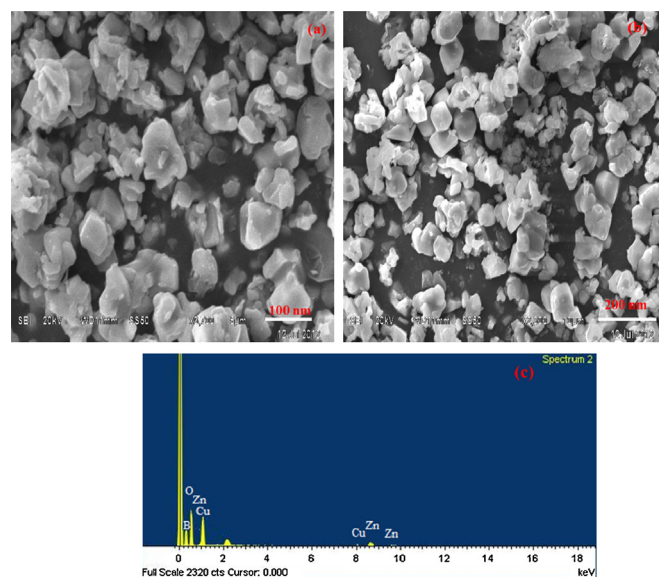


Fig. 2. (a and b) SEM images with different magnifications, (c) EDS spectrum of Cu^{2+} -doped zinc borate nanoparticles.

width at half maximum (FWHM) of the diffraction line and θ is the diffraction angle. Based on the FWHM values, the evaluated average crystalline size is 28 nm. The calculated average crystalline size of prepared sample almost matches with the value that is obtained from the TEM image.

The SEM images of Cu^{2+} -doped $\text{Zn}_3(\text{BO}_3)_2$ nanoparticles are shown in Fig. 2(a) and (b). The SEM images exhibited the surface morphology with different magnifications. From the figure, it is noticed that the surface morphology of the synthesized sample exhibit a spheres-like morphology. In many cases of crystalline materials, it is observed that there is a tendency of agglomeration among the nanoparticles [22]. The crystalline size evaluated from XRD studies do not match with the SEM images. This can be explained by the fact that the grains seen in the SEM images are the domains formed by aggregation of the nano size crystalline [23]. Elemental composition analysis of the prepared nanoparticles is carried out using energy dispersive spectroscopy (EDS). The EDX spectrum gives information about the chemical composition of the elements present from the surface to the interior of the solids, and they are used to confirm the homogeneity of the investigated sample. The EDX spectra of the copper ions doped zinc borate nanoparticles are shown in Fig. 2(c). From the EDX results, the spectrum indicated the presence of Zn, Cu, B, and O as the major elements in the synthesized sample. No other impurities peaks are observed from the EDX spectrum.

Fig. 3(a) and (b) shows the TEM microphotograph of the Cu^{2+} -doped zinc borate nanoparticles with different magnifications. The particles have a regular spheres-like structure. Which indicate the zinc borate particles are uniform in both morphology and particle size distribution. Fig. 3(c) shows the HRTEM image of Cu^{2+} -doped $\text{Zn}_3(\text{BO}_3)_2$ nanoparticles. A lattice fringes with spacing 0.234 nm observed from the HRTEM image, which corresponds to the (402) lattice plane of monoclinic phase. In order to examine the structure of prepared sample selected area electron diffraction (SAED) patterns and diffraction contrast image was taken, which is shown in Fig. 3(d). The diffracting planes are indexed as (202) and (402) reflections which are corresponding to the monoclinic phase of zinc borate, which is also observed from the X-ray diffraction pattern. The calculated particle size from the TEM is 30 nm, which is good agreement with the XRD measurement.

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