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Synthesis and Optical Characterizations of Vanadium Ions Doped Cadmium Borate Nano Powder

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Abstract: ***Vanadium doped cadmium borate nanopowder was synthesized at room temperature by chemical precipitation method. The prepared powder was characterized by Scanning Electron Microscopy (SEM), Electron paramagnetic resonance (EPR), Optical studies. SEM images show the irregular shaped stone like morphology of nanopowder. From EPR resonance, the spin Hamiltonian parameters are evaluated as $g_{\parallel}$ =1.9367 A= and $g_{\perp}$ = 1.9752. Optical absorption spectrum confirmed that the doped VO^{2+} ions are present in the nanopowder with distorted octahedral site symmetry. The evaluated bonding parameters revealed a partial covalent bonding between the doped ion and host lattice.***

Keywords: VO^{2+} doped $Cd_3(BO_3)_2$, SEM, EPR, Optical absorption spectroscopy

1. Introduction

Nano structured materials can be utilized in fabricating novel active devices with enhanced functionalities. Nanomaterials have potential to improve the environment through the development of new solutions to environmental problems [1,2]. **Transparent conducting oxides such as tin** oxide, indium oxide, doped zinc oxides and cadmium oxides have gained significant attention in recent years due to their high optical transmittance and low resistivity [3–5]. Cadmium oxide (CdO) is a II–VI group n-type compound semiconductor, it has a direct and indirect bandgap of 2.5, 1.98 eV respectively [6,7]. The major intentional uses of cadmium are Ni-Cd batteries, cadmium pigments, cadmium stabilizers, cadmium coatings, cadmium alloys and cadmium electronic compounds such as cadmium telluride (CdTe). For semiconductors, doping is a powerful tool to tailor the electrical and optical properties and more efforts have been devoted to investigate the doped counterparts. **There are several types of approaches about synthesizing nano-sized metal borates like thermal evaporation, a sol-gel process followed by annealing, supercritical ethanol drying technique and chemical vapor deposition. However, high temperatures are needed for these methods and to obtain hydrated nano sized metal borates, new methods have to be developed [8].**

Among inorganic materials, metal oxides such as cadmium borate play a fundamental role in developing new devices as they present a considera-ble variety of structures, stoichiometry's, chemical and physical properties that can be tailored to exploit a variety of suitable synthesis techniques**.** Borate compounds are well known remarkably for their use in industries and mineralogy. Metal borates have excellent mechanical properties, good chemical inertness and high stability under high temperature, lightweight, and low thermal expansion coefficients [9]. Recently optical and FT-IR studies of vanadium ions in cadmium borate glass and effects of gamma irradiation were reported by Abdul et al.,[10]. In this sequence we synthesized vanadium ions doped cadmium borate nanopowder by simple chemical precipitation method and is characterized by different spectroscopic methods.

2. Experimental:

2.1 Chemicals required:

Cadmium nitrate, Borax, Vanadium pentaoxide, and deionized water.

2.2 Procedure:

The vanadium doped cadmium borate nanopowders were produced from a solution of cadmium nitrate (0.1 M), borax (0.1 M) and vanadium pentaoxide (0.01 M) by using de-ionized water as solvent. The uniform magnetic stirring was provided for better atomic diffusion during reaction. The resulting precipitate was centrifuged by using ultracentrifuge and washed several times with de-ionized water. The precipitate was then dried in a hot air oven at 190-200 ^{0}C.

2.3 Characterization:

Scanning Electron Microscope images were taken from ZEISS EVO18. Optical absorption spectrum is recorded at room temperature on JASCO V-670 Spectrometer in the wave length region of 300-1000 nm. EPR spectrum is recorded at room temperature on JES-FA series X-band EPR Spectrometer having 100 KHZ field modulations.

3. Results and Discussion:

3.1 SEM:

Scanning electron microscopy is widely used to obtain information about the surface morphology of synthesized nanopowder. The synthesized nano powder morphology was shown in Fig.1. From SEM images, the formation of non-uniformly distributed irregular shaped stone like morphology was observed with below 50 nm of the VO^{2+} doped cadmium borate nanopowder.

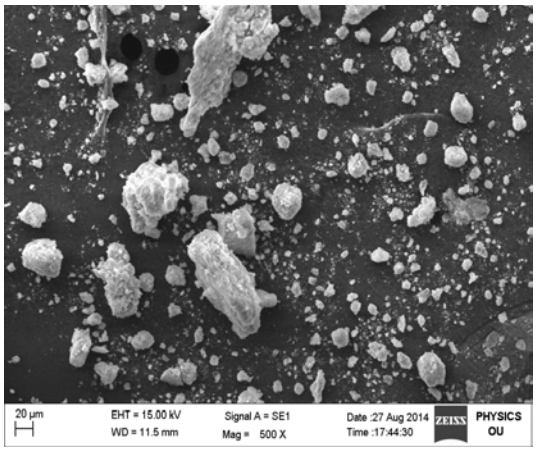

Fig.1 SEM image of VO^{2+} doped $Cd_3(BO_3)_2$.

3.2 Optical Analysis:

The optical absorption spectrum of VO^{2+} ion doped in cadmium borate nanopowder at room temperature (Fig.2.) showed three characteristic bands in the UV-Vis region. The band positions at 828 nm (12077 cm^{-1}), 643 nm (15552 cm^{-1}) and 422 nm (23696 cm^{-1}) are observed. In a C_{4v} symmetry environment, the ground state is an orbital singlet and the d electron is in the non-bonding ($^2B_{2g}$) type d_{xy} orbital. On the basis of molecular orbital theory, the observed bands are assigned to the transitions, $^2B_{2g} \rightarrow {}^2E_g$ ($d_{xy} \rightarrow d_{xzyz}$), $^2B_{2g} \rightarrow {}^2B_{1g}$ ($d_{xy} \rightarrow d_{x2-y2}$) and $^2B_{2g} \rightarrow {}^2A_{1g}$ ($d_{xy} \rightarrow d_z^2$) in increasing order of energy. The crystal field parameters (Dq) and tetragonal field parameters (Ds and Dt) are evaluated from the following expressions.

$$^2B_{2g} \rightarrow {}^2E_g = -3Ds + 5Dt$$

$$^2B_{2g} \rightarrow {}^2B_{1g} = 10Dq$$

$$^2B_{2g} \rightarrow {}^2A_{1g} = 10Dq - 4Ds - 5Dt$$

The evaluated values are: Dq = 1565, Ds = -2329, Dt = 1017 cm^{-1}. These parameters are in agreement well with the reported values of VO^{2+} ions [11-13] doped in different chemical environments.

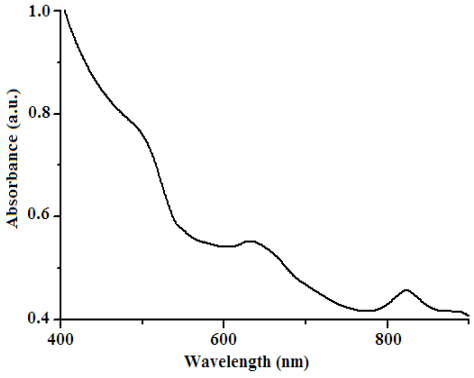

Fig.2. Optical spectrum of VO^{2+} doped $Cd_3(BO_3)_2$.

3.3 EPR analysis: The nanopowder EPR spectrum of VO^{2+} ions doped cadmium borate nanopowder sample is shown in Fig. 3. In this spectrum we have noticed eight line hyperfine patterns which are poorly resolved. It has been reported that the most common coordination of vanadium is octahedral with tetragonal distortions [14]. In present investigation, spin-Hamiltonian parameters ($g_\parallel$, $g_\perp$, and $A_\parallel$, $A_\perp$) are evaluated as $g_\parallel$ = 1.9367, $g_\perp$ =1.9752, $A_\parallel$ =320 x 10^{-4} cm^{-1}, $A_\perp$ = 101 x 10^{-4} cm^{-1}. An octahedral site symmetry with a tetragonal compression would give values of $g_\parallel < g_\perp < g_e$ and $A_\parallel > A_\perp$ [15].The values of spin-Hamiltonian parameters agree with the above condition. From this observation, it is suggested that the paramagnetic vanadyl ion in an octahedral

environment of oxygen with tetragonal distortion (C_{4v}). The dipolar coupling constant (P) and Fermi-constant coupling parameter (k) is evaluated using the formulae [16].

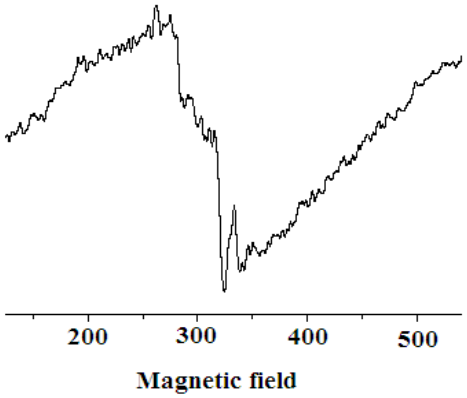

Fig.3. EPR spectrum of VO^{2+} doped $Cd_3(BO_3)_2$.

$$A_{\parallel} = P [- (4/7) - \kappa + (g_{\parallel} - g_e) + 3/7 (g_{\perp} - g_e)]$$

$$A_{\perp} = P [2/7 - \kappa + 11/4 (g_{\perp} - g_e)]$$

Here $g_e = 2.0023$. The evaluated values are: $\kappa = 0.89$, $P = 187 \times 10^{-4}$ cm^{-1} respectively. Both the EPR and optical data can used to calculate the molecular orbital bonding coefficients from the following equations.

$$\beta^{*2} = (g_e - g_{\parallel}) \Delta_{\parallel} / 8\lambda$$

$$\epsilon_{\pi}^{*2} = (g_e - g_{\perp}) \Delta_{\perp} / 2\lambda$$

Where 'λ' is the free ion value of spin orbit coupling constant for VO^{2+} ion and is equal to 170 cm^{-1}. From Optical absorption studies, the two bands (15552 and 12077 cm^{-1}) are typical for VO^{2+} and can be assigned to $\Delta_{\parallel} = {}^2B_{2g} \rightarrow {}^2B_{1g}$ and $\Delta_{\perp} = {}^2B_{2g} \rightarrow {}^2E_g$ transitions respectively. The evaluated values are $\beta^{*2} = 0.7548$ and $\epsilon_{\pi}^{*2} = 0.9626$. The values of β^{*2} coefficient shows partial covalent bonding nature of the Vanadyl ion with host material. The values of g, hyperfine coupling constant and bonding parameters are similar to the values reported for VO^{2+} containing of frame work materials in distorted octahedral site symmetry [17,18].

4. Conclusions:

VO^{2+} doped cadmium borate nanopowder is prepared by simple chemical precipitation method at room temperature. EPR and optical studies suggest a tetragonally distorted octahedral site symmetry environment of VO^{2+} ions in host lattice. The bonding parameters indicate the doping metal ion and host are in partial covalent bonding nature.

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