

Room temperature synthesis and spectral characterization of Cu²⁺-doped CdO powder

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Abstract: In the present study, we have synthesized undoped and Cu²⁺-doped CdO nanopowders by a mild solution method at room temperature. Powder X-ray diffraction, optical absorption, electron paramagnetic resonance and Fourier transform infrared measurements are used to characterize prepared powders. The powder X-ray diffraction patterns reflect the cubic crystal structure for undoped and Cu²⁺-doped CdO powders. Surface morphology images and compositional features are studied by scanning electron microscopy and energy-dispersive X-ray techniques, respectively. The optical absorption spectra exhibit a single absorption band for Cu²⁺-doped sample, which is the characteristic absorption band of distorted octahedral site symmetry. By correlating the electron paramagnetic resonance and optical results for Cu²⁺-doped CdO nanopowder, bonding parameters are evaluated. These values indicate the partial covalency of in-plane σ (α^2) and in-plane π bonding (β_1^2) between copper ions and their ligands. The FT-IR spectra indicate the fundamental vibrations of Cd–O.

Keywords: Optical materials; Electron paramagnetic resonance; X-ray diffraction; Crystal structure

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1. Introduction

The preparation and characterization of II–VI semiconductor particles have received significant attention due to their fundamental and technological importance. The changes in properties of the material depend upon two factors: first an increase in the surface-to-volume ratio and second an increase in the band gap energy due to change in the electronic structure [1]. When the nanoparticle is size-comparable to the excitonic Bohr radius, these particles show significant changes in their optical properties [2]. However, among the II–IV compounds, cadmium oxide (CdO) is a known n-type semiconductor with a direct band gap of 2.3–2.5 eV and an indirect band gap of 1.36–1.98 eV.

Due to its inherent non-stoichiometry, CdO exhibits high electrical conductivity and carrier concentration. CdO has been used in heat mirrors due to high reflectance in the

infrared region and relatively high transparency in the visible region. The unique combination of high electrical conductivity, high carrier concentration, and high transparency in the visible range of the electromagnetic spectrum has resulted in their applications in solar cells, chemical sensors, and liquid crystal displays [3–5].

The lattice unit cell compresses when dopant ions have radii smaller than that of doped materials [6]. However, the effect of the incorporation by ions of smaller ionic radii than that of Cd²⁺ on the optical and structural properties of CdO is still under investigation. Cu²⁺ ions at a certain concentration can improve the properties of CdO [7], since the ionic radius of Cd²⁺ ion (0.095 nm) is greater than that of Cu²⁺ ion (0.073 nm) [8].

Generally, optical properties are closely related to the local structure and dynamical behavior of the impurity in the host. Useful information about electronic states and local structures of paramagnetic impurities in crystals is obtained from electronic paramagnetic resonance (EPR) [9–11]. This information is helpful to understand optical properties of materials. Investigations of g and A factors and the local structure for Cu²⁺ centers are of significance

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[12]. Cu^{2+} -doped ZnCdO nanopowder has been prepared by using a mild and simple solution method. In case of ZnCdO, Cu^{2+} ions enter into the host lattice at single site, and in case of ZnO, Cu^{2+} ions enter into the host lattice at two different sites [12, 13]. Recently, undoped and Cu^{2+} -doped CdO nanopowders have been successfully synthesized by using a solid-state reaction method with the aid of the sonication process [14]. Solid-state reaction method, which requires generally high temperature, is a must in order to accelerate the slow solid–solid diffusion. This method also yields samples with low homogeneity, secondary phases, and uncontrolled (and typically large) particle size of low surface area [15, 16]. Solid-state reactions can only take place at the interface of two solids. A lot of energy may be required to break the bonds of the precursor. Mild solution method is a relatively simple method that is suitable for mass production. The preparation parameters such as the concentration and complexing agent are easily controllable [17].

Doping of a small concentration of a paramagnetic impurity into a diamagnetic host lattice helps detect the changes in the general characteristics of the host impurity. Cu^{2+} ion is the simplest paramagnetic probe that enters easily into a number of host lattices, and one gets an idea about the ground state (compressed/elongated octahedron), type of Jahn–Teller distortion (static/dynamic/tunneling), etc.

In view of above, in the present investigation, we have prepared undoped and Cu^{2+} -doped CdO powders by a mild and simple solution method at room temperature. The prepared powders have been characterized by structural and spectral investigations in order to obtain a comprehensive view of dopant ion oxidation, site symmetry, and the nature of the bonding between metal ion and its ligand.

2. Experimental details

The sample preparation was performed at room temperature in the presence of methanol. Cadmium nitrate $\text{Cd}(\text{NO}_3)_2$ and NaOH as a starting chemicals. A solution (20 mL) containing 0.1 M cadmium nitrate in methanol was added dropwise under stirring to 100 mL of 0.1 M NaOH in methanol and stirred for 30 min with a magnetic stirrer. The solution was then diluted by adding 120 mL of methanol. Then, a mixture of methanol and water in the ratio of 0.004 was used for undoped CdO powder. For the preparation of Cu^{2+} -doped CdO powder, 0.1 mol % of copper nitrate was added to the above solution and it was stirred for 30 min until a clear solution was obtained. The obtained solution was stored in a refrigerator for 2 h. It was then filtered and dried in air at room temperature.

X-ray diffraction patterns of the powder samples were recorded using a PANalytical X-Pert Pro-diffractometer

with CuK_α radiation (1.5406 Å). The morphology of the fine powder samples was recorded on a Carl Zeiss SEM EVO with a carbon coating. The EDX pattern was recorded on an Oxford Penta FET. Optical absorption spectra of the samples mixed with liquid paraffin were recorded using a JASCO V670 UV–VIS–NIR spectrophotometer in the region of 200–1400 nm. EPR spectrum was recorded on an FE1X 100 EPR spectrometer at room temperature. FT-IR spectra were recorded on a Thermo Nicolet 6700 spectrometer in the range of 4000–400 cm^{-1} .

3. Results and discussion

The powder X-ray diffraction (XRD) patterns of undoped and Cu^{2+} -doped CdO powders are shown in Fig. 1. The observed intense peaks from X-ray diffraction patterns are in good agreement with reported data (JCPDS File No. 75-0592). Due to the dopant ion in the CdO, a slight shift in diffraction peaks has been observed. All of the reflections can be assigned to the standard powdered pattern for the pure cubic phase of CdO with a lattice constant of $a = 0.4679$ nm. Lattice cell parameter of bulk CdO is 0.4694 nm. The decrease in the lattice constant is due to the substitution of Cd^{2+} by smaller Cu^{2+} ions [14–19]. The ionic radii of Cu^{2+} and Cd^{2+} are 0.73 and 0.95 Å, respectively. Since copper has a smaller radius than that of cadmium, it may be easy for it to diffuse into the host lattice, while causing a slight mismatch, which induces the slight angle shift, mentioned above.

The average crystalline size of prepared powders has been calculated using Scherrer's formula, using the full-width at half-maximum (FWHM) intensity:

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

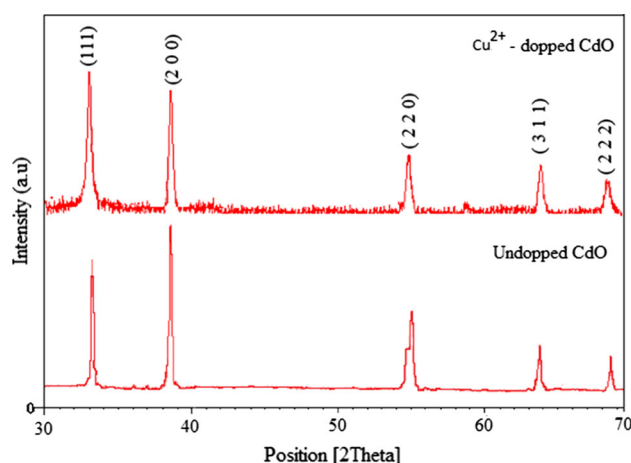


Fig. 1 Powder XRD patterns of undoped and Cu^{2+} -doped CdO powders

where t is the thickness in nm, λ is the wavelength of X-rays used (1.5406 \AA), β is the FWHM, and θ is the angle of diffraction. The evaluated average crystalline sizes are 90 and 85 nm, respectively, for undoped and Cu^{2+} -doped CdO powders.

SEM images of prepared undoped and Cu^{2+} -doped sample powders are shown in Fig. 2(a) and 2(b). The particle size is in a few micron ranges and exhibits flower-like structure for undoped CdO nanopowder (Fig. 2(a)) and irregular-shaped stone-like structure for Cu^{2+} -doped CdO nanopowder (Fig. 2(b)). It can be seen that grains clump together and hence display homogeneous distribution for undoped and not show homogeneous distribution for Cu^{2+} -doped CdO powders. The EDX spectra of undoped and Cu^{2+} -doped CdO powders are shown in Fig. 2(c) and 2(d). The EDX data indicate the distribution of Cd, Cu, and oxygen species with chemical composition mapping.

The optical absorption spectra of undoped and Cu^{2+} -doped CdO nanopowders are shown in Fig. 3. No absorption peak has been observed for undoped CdO [14]. In octahedral crystal fields, only one single-electron transition is expected for Cu^{2+} . 2E_g splits into ${}^2B_{1g}$ ($d_{x^2-y^2}$) and ${}^2A_{1g}$ (d_z^2) levels, where ${}^2B_{1g}$ is the ground state. The upper state ${}^2T_{2g}$ splits into ${}^2B_{2g}$ (d_{xy}) and 2E_g (d_{xz}, d_{yz}). Due to Jahn–Teller distortion, energy levels split [20] predominantly into an elongated octahedral coordination with four short in-plane bond lengths and two longer axial bond lengths [20]. Accordingly, three transitions, ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and ${}^2B_{1g} \rightarrow {}^2E_g$, are expected. But only a single optical absorption maximum is observed in most of

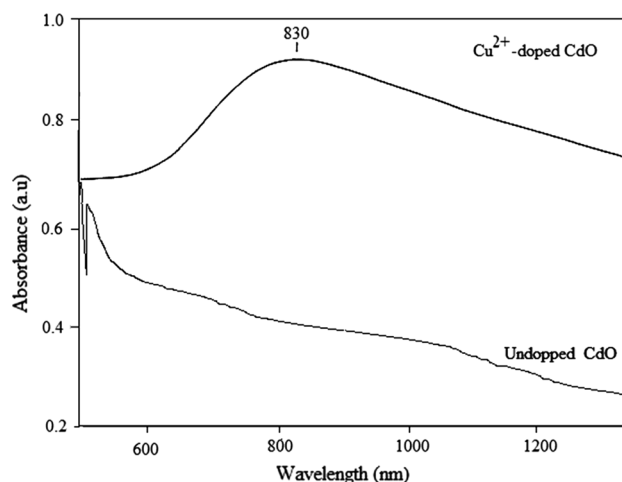
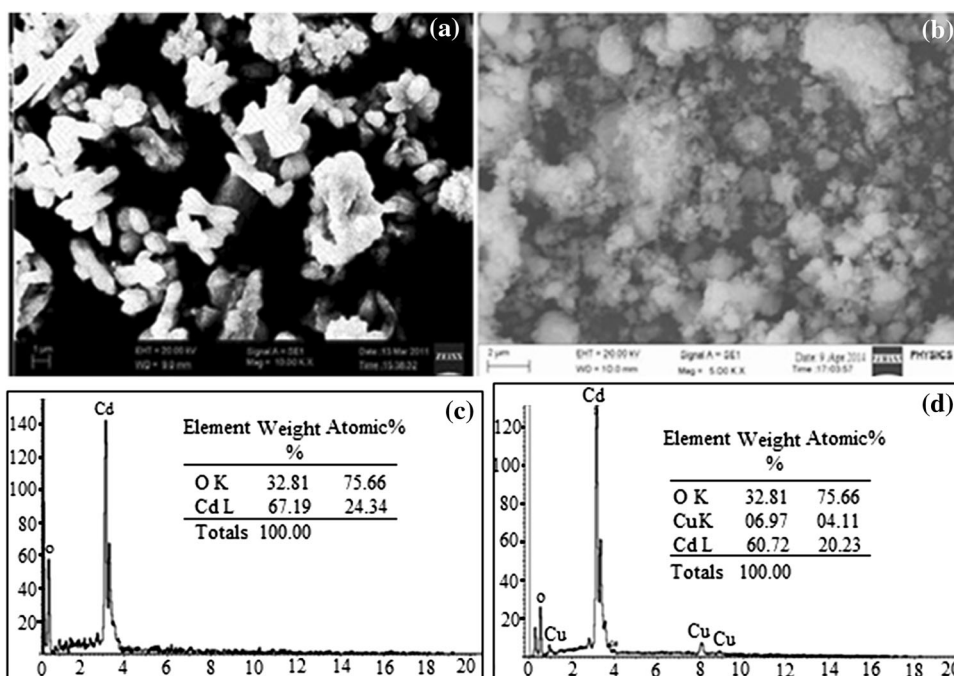


Fig. 3 Optical absorption spectra of undoped and Cu^{2+} -doped CdO powders

the cases [21]. This single optical band has been interpreted as the overlap of all three transitions [22, 23]. In the present investigation, a broad band is observed at 830 nm ($12,044 \text{ cm}^{-1}$), which is the characteristic absorption band of distorted octahedral site symmetry [22]. Thus, the band is assigned to the ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transition. Similar results have been observed for Cu^{2+} -doped materials, as reported in the literature [24, 25]. The distortion is due to the cubic symmetry of Cu^{2+} ions disturbed by electronic hole in the degenerated orbital. According to the Jahn–Teller theorem, any nonlinear system with a degenerate ground state should distort in order to eliminate the degeneracy. So two

Fig. 2 SEM images of (a) undoped and (b) Cu^{2+} -doped and EDX spectrum of (c) undoped and (d) Cu^{2+} -doped CdO powders



structural changes may be possible, one is elongated and another is compressed structure [26]. In the present study, Cu^{2+} ions are in octahedral site symmetry with elongated distortion.

For Cu^{2+} ions, a regular octahedral site may not exist as the cubic symmetry is disturbed by the electronic hole in the degenerate $d_{x^2-y^2}$ orbital that produces the tetragonal distortion. No EPR spectrum is observed for undoped CdO nanopowder at room temperature. The EPR spectrum of the Cu^{2+} -doped CdO powder is shown in Fig. 4. The EPR spectrum (Fig. 4) exhibits two sets of hyperfine lines: parallel and perpendicular. The evaluated spin-Hamiltonian and hyperfine splitting parameters are $g_{\parallel} = 2.328$, $g_{\perp} = 2.069$ and $A_{\parallel} = 156 \times 10^{-4} \text{ cm}^{-1}$, $A_{\perp} = 38 \times 10^{-4} \text{ cm}^{-1}$. The evaluated spin-Hamiltonian parameters in the present study are in good agreement with these reported earlier [27, 28]. $g_{\parallel} > g_{\perp} > 2.0023$, which indicates that the Cu^{2+} has an octahedral environment elongated along one of the cubic axes and the ground state is $d_{x^2-y^2}$. ($g_{\parallel} > g_{\perp}$ suggests that Cu^{2+} ions are subjected to a tetragonally elongated distorted octahedron).

The dipolar term (P) and the Fermi contact term (κ) have been calculated from spin-Hamiltonian parameters using following expressions [29, 30]:

$$P = 2\gamma_{\text{Cu}}\beta_o\beta_N\langle r^{-3} \rangle = 0.036 \text{ cm}^{-1} \quad (2)$$

$$\kappa = (A_o/P) + \Delta g_o \quad (3)$$

where γ_{Cu} is the magnetic moment of copper, β_o is the Bohr magneton, β_N is the nuclear magneton, and r is the distance from the central nucleus to the electron. $A_o = (A_{\parallel} + 2A_{\perp})/3$, where A_{\parallel} and A_{\perp} are the hyperfine coupling constants in parallel and perpendicular directions to the field, respectively. g_{\parallel} and g_{\perp} are values parallel and perpendicular to the field, respectively, and $\Delta g_o = g_o - g_e$, where $g_o = (g_{\parallel} + 2g_{\perp})/3$ and g_e is the free ion g value (2.0023). The Fermi contact term κ is a measure of the polarization produced by the uneven distribution of d-electron density on the inner core s-

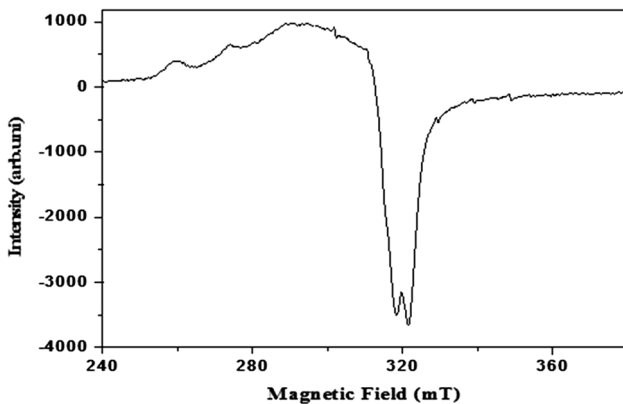


Fig. 4 EPR spectrum of Cu^{2+} -doped CdO powder ($\nu = 9.151 \text{ GHz}$)

electron. The evaluated κ value (0.368) is in agreement with the general order [31]. The covalency parameter for in-plane σ -bonding has been evaluated using the following expression [32]:

$$\alpha^2 = \frac{A_{\parallel}}{0.036} + (g_{\parallel} - g_e) + \frac{3}{7}(g - g_e) + 0.04 \quad (4)$$

The value of α^2 thus evaluated is 0.83 and the value of α is 0.911. α^1 can be evaluated from the normalization conditions on the ground-state b_1 orbital as follows:

$$\alpha' = (1 - \alpha^2)^{1/2} + \alpha S \quad (5)$$

where S is the overlap integral between the $d_{x^2-y^2}$ orbital and the normalized ligand orbital. In case of oxygen ligands, the value of $S = 0.076$ [24]. In the present investigation, the atom surrounding the copper ion is oxygen, so the evaluated value of α^1 is 0.484. By correlating the EPR and optical absorption data, the bonding parameter β_1 is calculated using the following expression:

$$g_{\parallel} = 2.0023 - 8\rho[\alpha\beta_1 - (1/2)\alpha'(1 - \beta_1^2)^{1/2}T(n)] \quad (6)$$

where $\rho = (\lambda_o\alpha\beta_1/\Delta E)$ and $T(n)$ is a function involving metal–ligand hybridization constant and the effective nuclear charges for the ligand 2s, 2p orbitals and the metal ion 3d orbitals and is equal to 0.22. ΔE is the transition energy between ${}^2B_{1g} \rightarrow {}^2B_{2g}$, and λ_o is the spin–orbit coupling constant (-828 cm^{-1}). The evaluated value of β_1^2 is 0.762.

From the calculated parameters α^2 and β_1^2 , the basicity of the oxide ion can be calculated. α^2 refers to the covalency of the in-plane π -bonding between copper and its ligands. α^1 is a parameter for normalization of the b_1 orbital and indicates the extent of overlap between the $d_{x^2-y^2}$ orbital of the central metal ion and the normalized ligand orbital. This intermediate parameter is used to evaluate another important parameter, β_1^2 , which is a direct measure of the covalency of the in-plane π -bonding between copper and its ligands. Since only one band is observed in optical absorption spectrum, the nature of the out-of-plane π -bonding can not be inferred [33]. The β_1^2 parameter is more sensitive to variations in the normalized covalency of Cu^{2+} -O in-plane bonding of σ , or π symmetry, and is expressed as follows [34]:

$$\Gamma_{\sigma} = 200(1-S)(1-\alpha^2)/(1-2S) \% \quad \text{and} \quad (7)$$

$$\Gamma_{\pi} = 200(1-\beta_1^2) \%$$

where the normalized covalency (Γ_{π}) of Cu^{2+} -O bonding of π symmetry indicates the basicity of the oxide ion. Generally, the covalency of the in-plane σ -bonding (Γ_{σ}) decreases and the covalency of in-plane π -bonding (Γ_{π}) increases. The evaluated values are $\Gamma_{\sigma} = 37.5 \%$ and

$\Gamma_{\pi} = 51.5\%$, respectively, and is therefore a better indicator of the covalent character.

The FT-IR spectra of undoped and Cu^{2+} -doped CdO powders are shown in Fig. 5. The band observed at 440 cm^{-1} indicates the transformation of $\text{Cd}(\text{NO}_3)_2$ to CdO is complete. The band observed at 860 cm^{-1} suggests the formation of the tetrahedral coordination of cadmium oxide [35]. The band observed at 2922 cm^{-1} is attributed to C–H (alkyl group) stretching band [36], and band at 716 cm^{-1} is attributed to the C–H (aromatics). The stretching mode of vibration of C=O is observed at 1435 cm^{-1} . The band at 1800 cm^{-1} is attributed to H–O–H symmetric bending, which represents the sample consists of crystal water [37]. The weak vibration of CO_2 band is observed at 2472 cm^{-1} . A band observed at 3612 cm^{-1} is ascribed to the symmetric stretching mode of H–O–H.

4. Conclusions

Undoped and Cu^{2+} -doped CdO powders are prepared by a simple mild solution method at room temperature and are characterized by various spectroscopic techniques. XRD patterns data indicate a cubic crystal structure. EPR spectrum exhibits resonance signals at $g = 2.328$ and 2.069 . These values indicate the characteristic of Cu^{2+} ions in tetragonally elongated octahedral sites. The evaluated spin-Hamiltonian and hyperfine splitting values indicate that the ground state of Cu^{2+} is $d_{x^2-y^2}$. The splitting factor ($g_{\parallel} - g_{\perp}$) indicates that the distortion is less in the case of CdO. The molecular orbital values are evaluated by correlating EPR and optical absorption data. The evaluated values of α^2 and β_1^2 obtained in the present study indicate that in-plane σ -bonding is moderately covalent and in-plane π -bonding is ionic in nature. The parameters Γ_{σ} (37.5%) and Γ_{π} (51.5%) are in accordance with the

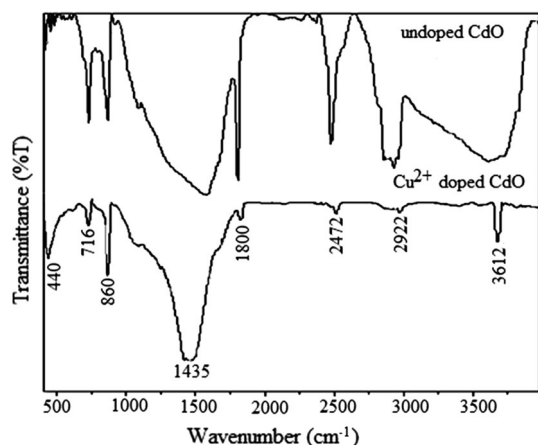


Fig. 5 FT-IR spectra of undoped and Cu^{2+} -doped CdO powders

expected basicity character of the complexes. FT-IR spectra show characteristic vibrations of the Cd–O molecule.

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