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Single-oscillator model and determination of optical constants of some optical thin film materials

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Abstract

The optical properties of some optical thin film materials have been investigated by means of the optical transmittance and reflectance spectra. The dispersion of the refractive index is discussed in terms of the Wemple–DiDomenico single oscillator model. The optical band gap values were calculated for Taue model and Wemple–Didomenico model. The optical band gaps which turned out to depend significantly on the metal coordination were calculated in terms of Taue method and Wemple–Didomenico model. The $E_{\mathrm{opt}}^{\mathrm{WD}}$ values obtained from Wemple–Didomenico model are in agreement with those determined from the Taue model. The type of optical transition responsible for optical absorption is indirect transition with an energy gap of 2.12–2.39 eV. The dispersion energies E_{d} of the thin films are in the range of 29.69–14.32 eV. The real and imaginary parts of the dielectric constant of the films were determined. The real and imaginary parts follow the same pattern and it is seen that the values of real part are higher than imaginary parts.

Keywords: Optical materials; Dispersion of refractive index; Optical band gap

1. Introduction

As is known, Schiff bases from the condensation of salicylaldehyde with alkyl and arylamines are known as *N*-alkyl or *N*-aryl salicylaldimines and widely used in coordination chemistry [1] which coordinates as deprotonated or neutral forms. The ortho-hydroxy Schiff bases form the intra-molecular hydrogen bonds and they are interesting ligands. Several adducts of non-transition, early transition and f-metals with such bases acting as neutral ligands [2] have been studied. Thiazoles represent a very interesting class of thin films because of their wide applications in pharmaceutical, phytosanitary, analytical, and industrial aspects, e.g. as fungicides, anthelmintics and

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herbicides [3]. On the other hand, cyclobutane carboxylic acids in different forms were described as highly potent l-Glutamate, N-methyl-D-aspartate (NMDA) agonist, NMDA antagonists and anticonvulsive drugs [4,5]. However, the syntheses and complexation properties of 1,1,3-trisubstituted cyclobutane-substituted thiazoles and their Schiff base derivatives containing the mesityl group have not been reported so far. Recently, there has been considerable interest in the chemistry of Schiff base compounds containing thiosemicarbazones and their metal complexes due to their biological activities [6] and nonlinear optical properties [7]. These compounds, containing cyclobutane, thiazole and Schiff base functions in their molecules, seem to be suitable candidates for further chemical modifications and may be optical communication and optical devices. Therefore, the optical absorption spectra have proved to be very useful for elucidation of the electronic structure and optical constant of these materials. Transition metal complexes have a number of electrical properties in the dark which similar to those of classic crystalline and amorphous semiconductors and these compounds can behave like intrinsic semiconductors. Optical and electrical properties of the metal complexes have become an increasingly interesting area of semiconducting and optical materials because these materials possess great potential for device applications such as Schottky diode, solid state devices and optical sensor. The study of optical absorption of transition metal complexes, particularly the absorption edge has proved to be very useful for elucidation of the electronic structure of these materials [8]. It is possible to determine indirect and direct transition occurring in the band gap of the metal complexes by optical absorption spectra [8]. The optical constants such as refractive index, absorption index and dielectric constant can be analyzed by transmittance and reflectance spectra.

In the present work, we are to investigate optical properties of some optical thin materials-based metal complexes so that this information would be helping the researchers toward applying these materials in optical communication and optical devices.

2. Experimental

2.1. Synthesis of the compounds

The ligand LH (0.2028 g, 0.50 mmol) was dissolved in absolute ethanol (15–20 mL). A solution of 0.25 mmol of the metal salt [$Co(AcO)_2 \cdot 4H_2O$ (0.0623 g), $Cu(AcO)_2 \cdot H_2O$ (0.0499 g), $Ni(AcO)_2 \cdot 4H_2O$ (0.0623 g) $Zn(AcO)_2 \cdot 2H_2O$ (0.0549 g)] in ethanol (10 mL) was added dropwise with continuous stirring. In the case of Co(II) complexes, a slow stream of nitrogen was passed through the solution. Every mixture was refluxed for 1 h and then left to stand overnight at room temperature. The complexes, precipitated as microcrystal, were filtered, washed with cold ethanol and water several times and dried in vacuum at 60 °C (over P_4O_{10}) and stored in a desiccator over $CaCl_2$. The synthesized complexes were characterized and described elsewhere [9]. The chemical structure of the complexes is given in Fig. 1. The solution of the films was homogenized for 5 h and was rotated for homogeneous mixing. Then, the thin films deposited on quartz substrates were prepared by evaporating the solvent from a solution of the compounds. The sum of transmittance and reflectance spectra in the transparent region was found as 100% within experimental error for the films. Thus, the homogeneity of the films was confirmed by these results [10]. The crystal structure of the films was studied

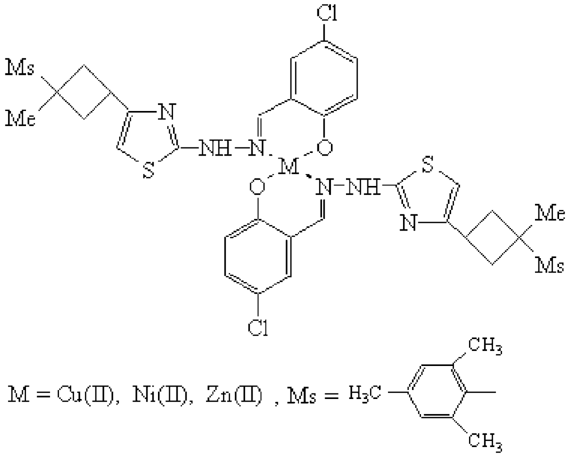

Fig. 1. The chemical structure of the compounds.

by X-ray diffraction study. But, any peak is not observed in the X-ray pattern. This confirmed that the films have amorphous structure. From the measured spectral curves, the average thicknesses of the films were determined using optical spectral curves of the films [11]. The values of film thickness of the Co(II), Ni(II), Cu(II) and Zn(II) films were approximately found as 588, 586, 584 and 582 nm, respectively. UV–Vis spectra of the thin films having different thicknesses were recorded at room temperature using a CECIL CE-5502 UV–Vis instrument.

3. Results and discussion

3.1. Optical absorption at the fundamental edge

Figs. 2(a, b) show the transmittance and reflectance spectra of the thin films as a function of wavelength. The absorption coefficient α was calculated using the well-known formula, $\alpha = -1/d\ln[T/(1-R)^2]$. The experimental results show that the dominant transition is the indirect one by the proposed Taue [12]. Thus, the plots of $(\alpha h\nu)^{1/2}$ vs. $h\nu$ were plotted to obtain optical band gaps of the thin films, as shown in Fig. 3. As a result of indirect transition, Eq. (1) is determined as,

$$(\alpha h\nu)^{1/2} = A(h\nu - E_{\mathrm{opt}}). \quad (1)$$

Indirect gap was determined from the linear portions as shown in figures and the values are given in Table 1. When the optical band gaps were compared with each other, their order follows $\mathrm{Zn(II)}_{E_{\mathrm{opt}}} < \mathrm{Ni(II)}_{E_{\mathrm{opt}}} < \mathrm{Co(II)}_{E_{\mathrm{opt}}} < \mathrm{Cu(II)}_{E_{\mathrm{opt}}}$. It is observed that E_{opt} values follow a certain trend except for Cu(II) sample and they decrease with increasing atomic number of the metal ion in the compounds, in which the atomic number follows the order of Co(II) < Ni(II) < Cu(II) < Zn(II). This suggests that the atomic number of metal ion dominates on the optical band gaps of the films, if the materials studied have the same coordination geometry. It is evaluated that the materials studied except for Cu(II) sample have tetrahedral geometry. Thus, we suggest that the metal coordination is dominant on the optical band gaps.

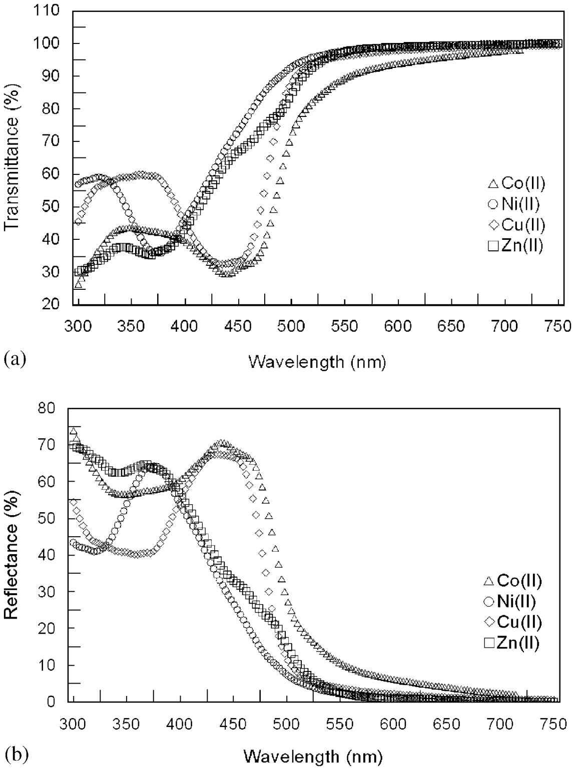

Fig. 2. (a) The transmittance and (b) reflectance spectra of the thin films.

The absorption edge can be determined from the exponential dependence of the absorption coefficient and it is determined as [13],

$$\alpha(h\nu) = \alpha_o \exp(h\nu/E_u), \quad (2)$$

where α_o is a constant and E_u is the Urbach energy. Plotting the dependence of ln α vs. $h\nu$ as shown in Fig. 4 should give a straight line. The E_u values were calculated from the following relationship,

$$E_u = \left(\frac{\mathrm{d}\ \ln\ \alpha}{\mathrm{d}\, h\nu}\right)^{-1}. \quad (3)$$

The steepness parameter, $\sigma = kT/E_u$, characterizing the broadening of the optical absorption edge due to electron phonon or exciton–phonon interactions [14] was also determined taking $T = 300$ K and given in Table 1. The σ values of the samples except for Cu(II) sample change inversely with optical band gaps. The atomic number of the metal ion causes a shift in the optical absorption edge therefore change in the band structure of the films. It is found that the optical absorption edge of the films except for Cu(II) decreases with increasing atomic number of the metal ion. The atomic number is responsible for the width of localized states in the optical band of the films and it decreases the width of localized states in the optical band gap. That is why, the σ values change inversely with optical band gaps of the films.

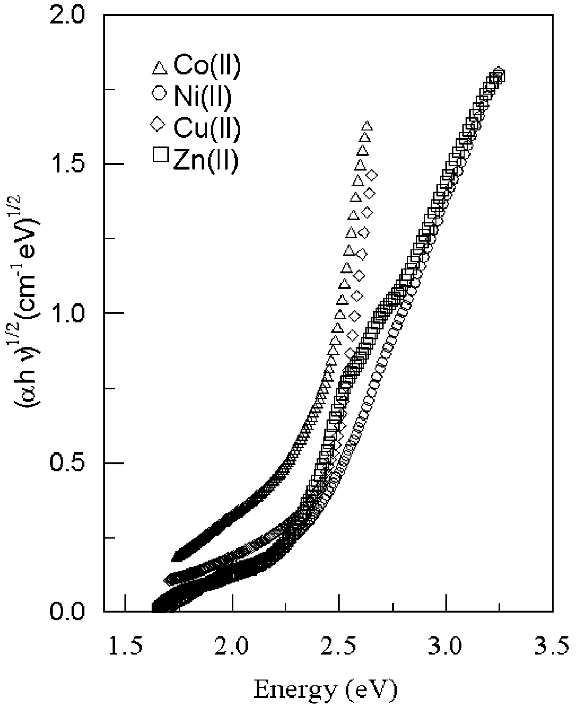

Fig. 3. The $(\alpha h\nu)^{1/2}$ vs. $h\nu$ plots of the thin films.

3.2. *Dispersion behavior of refractive index*

We determined values of n and k from the transmittance and reflectance spectra of the thin films. The reflectance spectra of the thin films exhibit a peak at energies to the interband transitions. The reflectance and refractive index of any solid certain constant wavelength are expressed as [15],

$$k = \frac{\alpha\lambda}{4\pi}, \tag{4}$$

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2}. \tag{5}$$

The spectral curves of n values determined using above relationships are shown in Fig. 5. As seen, n values increase with increasing photon energy and

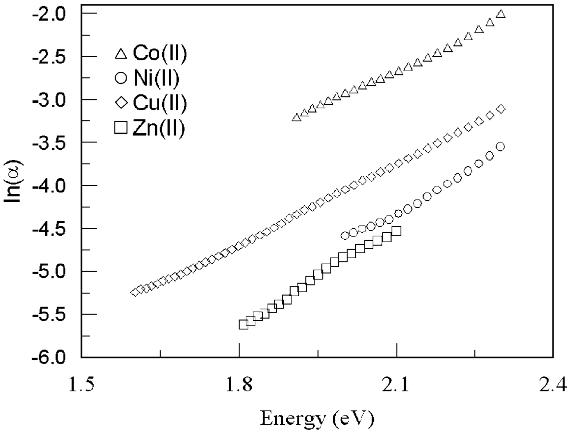

Fig. 4. The Urbach plots of the thin films.

Table 1
The optical parameters of the thin films

Film	$E_{\mathrm{opt}}{}^{T}$(eV)	$E_{\mathrm{opt}}^{\mathrm{WD}}$(eV)	E_{u} (meV)	σ	E_{o} (eV)	E_{d} (eV)	n_∞	λ_{o} (nm)	S_{o} (m^{-2})
Co(II)	2.30	2.15	347.7	0.071	4.30	18.52	4.99	288.3	$5.06\ 10^{13}$
Ni(II)	2.25	2.41	287.4	0.086	4.82	14.32	2.35	270.7	$1.69\ 10^{13}$
Cu(II)	2.39	2.46	322.6	0.077	4.94	29.69	2.73	281.1	$2.15\ 10^{13}$
Zn(II)	2.12	2.24	253.6	0.098	4.48	23.6	6.35	276.7	$7.43\ 10^{13}$

$E_{\mathrm{opt}}{}^{T}$ (eV) optical band gap obtained from the Taue model, $E_{\mathrm{opt}}^{\mathrm{WD}}$ (eV) optical band gap obtained from the Wemple–Didomenico model, E_{u} (meV) width of the localized states obtained from the Urbach plot, σ steepness parameter, E_{o} (eV), the oscillator energy, E_{d} (eV), the dispersion energy, n_∞ the long wavelength refractive index, λ_{o}(nm) average interband oscillator wavelength and S_{o} (m^{-2}) the average oscillator strength.

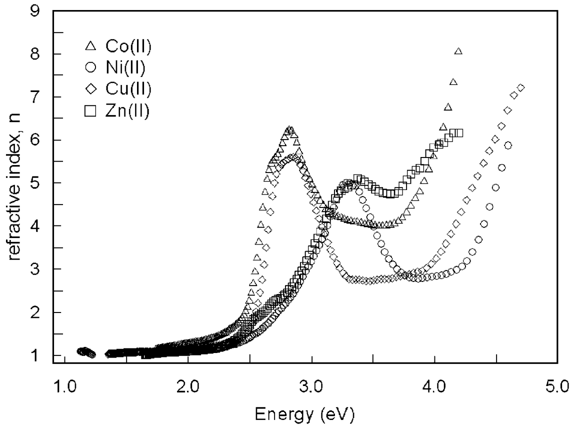

Fig. 5. The refractive index plots of the thin films.

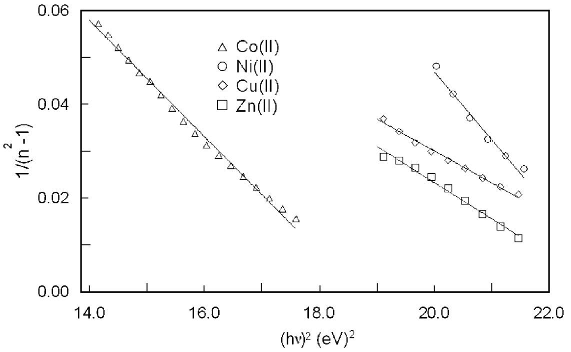

Fig. 6. The $1/(n^2-1)$ vs. $(h\nu)^2$ plots of the thin films.

the refractive index values of the thin films shows significant differences. This is due to the major contribution of virtual electronic transitions in the thin films. This leads to a significant change in the optical parameters. In the interband region there is appreciable modification of the photon energy dependence of the refractive index. A peak is observed in the refractive index spectra of the compound and shifts toward higher photon energies. The refractive index dispersion of the compounds studied can be fitted by the Wemple–-DiDomenico relationship. The dispersion plays an important role in the research for optical materials, because it is a significant factor in optical communication and in designing devices for spectral dispersion. The result of refractive index dispersion below the interband absorption edge corresponds to the fundamental electronic excitation spectrum. Thus, the refractive index is related to photon energy through the relationship [16,17],

$$n^2 = 1 + \frac{E_o E_d}{E_o^2 - (h\nu)^2}, \tag{6}$$

where E_o and E_d are single-oscillator constants. We calculated the values of the parameters E_o and E_d by plotting $(n^2-1)^{-1}$ vs. $(h\nu)^2$ (Fig. 6) and they are given in Table 1. The parameter E_d is the oscillator strength or dispersion energy which is a measure of the strength of interband optical transitions. The oscillator energy E_o is an average energy gap. Furthermore, an approximate value of the optical band gap, E_{opt}, can be obtained from the Wemple–Didomenico model. The optical band gap values, E_{opt}, were also calculated from the Wemple–DiDomenico dispersion parameter, E_o, using $E_{opt} \approx E_o/2$ relationship [18,19]. The E_{opt}^{WD} values obtained from Wemple–Didomenico model are in agreement with those determined from the Taue model (see Table 1).

The long wavelength refractive index (n_∞), average interband oscillator wavelength (λ_o) and the average oscillator strength (S_o) for the thin films were determined using the following relationship [20],

$$\frac{(n_\infty^2 - 1)}{(n^2 - 1)} = 1 - \left(\frac{\lambda_o}{\lambda}\right)^2, \tag{7}$$

where (n_∞) and (λ_o) values were calculated from the plots of (n^2-1) vs. λ^{-2} and are given in Table 1. Eq. (7) can also be written as,

$$n^2 - 1 = \frac{(S_o \lambda_o^2)}{(1 - \lambda_o^2/\lambda^2)}, \tag{8}$$

where $S_o = (n_\infty^2 - 1)/\lambda_o^2$. The E_o and S_o values were obtained using above equation and are given in Table 1. These values are of the same order as those obtained by DiDomenico and Wemple [20] for a number of materials.

3.3. Complex dielectric constant

The real and imaginary parts of the dielectric constant can be given in the following form [21];

$$\varepsilon_1 = n^2 - k^2 \quad \text{and} \quad \varepsilon_2 = 2nk. \tag{9}$$

The dependences of ε_1 and ε_2 on photon energy are shown in Figs. 7(a, b). The real and imaginary parts follow the same pattern and it is seen that the values of real part are higher than imaginary parts. The variation of the dielectric constant with photon energy indicates that some interactions between photons and electrons in the films are produced in this energy range. These interactions are observed on the shapes of the real and imaginary parts of the dielectric constant and they cause formation of peaks in dielectric spectra. This formation depends on the type of the compound. The maximum peak height of these peaks corresponds to plasma frequency.

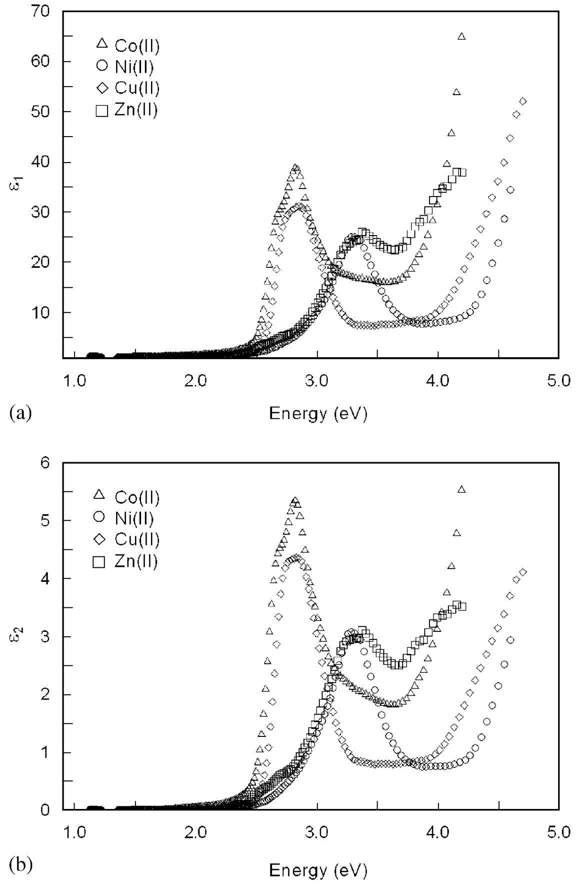

Fig. 7. The dielectric constant plots of the thin films: (a) real part; (b) imaginary part.

4. Conclusions

On the basis of the optical investigations of the films, the following results were obtained. The optical band gaps which turned out to depend significantly on the metal coordination were calculated in terms of Taue method and Wemple–Didomenico model. The $E_{\mathrm{opt}}^{\mathrm{WD}}$ values obtained from Wemple–Didomenico model are in agreement with those determined from the Taue model. The type of optical transition responsible for optical absorption was indirect transitions. The optical constants (refractive index n, extinction coefficient k and dielectric constant) were analyzed from the transmittance and reflectance spectra. The spectral dependence of the optical curves indicates that the optical parameters change with metal coordination in the films.

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