

# Optical characterization of an amorphous organic thin film

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The optical characteristics of Co(II) complex having 5,6-O-cyclohexylidene-1-amino-3-azahexane thin film were investigated by spectrometric measurements. The optical parameters, optical band gap  $E_g$  and width of localized states  $E_o$  of the film were determined using the transmittance  $T$  and the reflectance  $R$  at normal incidence in the spectral range 540–660 nm. The absorption edge of the film exhibits the exponential behavior which is attributed to the electronic transition in the localized states tailed off in the indirect energy band gap of the film. The refractive index spectra of the film show normal dispersion up to about 2 eV and afterwards, the refractive index increases with increasing photon energy.

Keywords: thin film, optical constants, optical band gap.

## 1. Introduction

Transition metal complexes have a number of electrical properties in the dark which are 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. It is possible to determine indirect and direct transition occurring in the band gap of metal complexes by optical absorption spectra [1–3]. The data transmittance and reflectance can be analyzed to determine optical constants such as refractive index, absorption index and dielectric constant. The refractive index is one of the fundamental properties of a material, because it is closely related to the electronic polarizability of ions and the local field inside the material. The evaluation of refractive indices of optical materials is of considerable importance for applications in integrated optical devices such as switches, filters and modulators, *etc.*, where the refractive index of a material is the key parameter for device design [4].

In the Ph.D. Thesis of YAKUPHANOGLU [5], temperature dependence of the electrical conductivity, thermal conductivity, crystal structure, microstructure and optical properties of new semiconducting metal complexes have been investigated. We evaluate that the synthesis of new metal complexes is considerably important for the development of semiconducting and optical materials. Studies on their optical properties have attracted much attention in the view of their application in optical communication and optical devices. Thus, the aim of this study is to obtain new optical materials and investigate optical properties to determine the optical constants such as refractive index, extinction coefficient and dielectric constant. The study of optical absorption, particularly the absorption edge has proved to be very useful for elucidation of the optical properties of these materials.

## 2. Experimental

### 2.1. Synthesis of 5,6-O-cyclohexylidene-1-amino-3-azahexane (ligand)

In a reaction flask containing a thermometer, a CaCl<sub>2</sub> drying tube and a dropping funnel, 13.20 mL (0.22 mole) of 1,2-diaminoethane, 8.0 mL (0.057 mole) of triethylamine and 60 mL absolute xylene were mixed. To this solution, a solution of 13.3 g (0.07 mole) of 1-chloro-2,3-O-cyclohexylidene propane in 25 mL xylene was added dropwise with continuous stirring. Then the mixture was further refluxed at 122–130°C for 30 h and cooled down to room temperature under nitrogen atmosphere. The precipitated triethylammonium salts was filtered and the filtrate was evaporated to remove the excess 1,2-diaminoethane. The compound was distilled at 134–145°C at 4 mm-Hg. Yield: 9.6 g (72.0%). Characteristic IR bands (NaCl cell, cm<sup>-1</sup>): 3392–3285; 1560 cm<sup>-1</sup>  $\nu$ (-NH and -NH<sub>2</sub>), 2980–2895 cm<sup>-1</sup>  $\nu$ (aliph. C-H), 1114 cm<sup>-1</sup>  $\nu$ (C-O-C). Characteristic <sup>1</sup>H NMR peaks (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 4.06 (1H, *p*, -CH-O), 3.88–3.56 (2H, *t*, -CH<sub>2</sub>-O), 2.57–2.69 (6H, *m*, -CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>), 1.32–1.48 (13H, *m*, cyclo-CH<sub>2</sub>, -CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>). Characteristic <sup>13</sup>C NMR resonances (400 MHz, CDCl<sub>3</sub>,  $\delta$  ppm): 23.84, 23.68, 25.12, 34.77 and 35.02 (5C, cyclo-CH<sub>2</sub>), 109.80 (1C, cyclo-CH<sub>2</sub>), 67.36 (-CH<sub>2</sub>-O), 75.42 (-CH-O), 72.83 (-CH<sub>2</sub>-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>), 52.65 (-NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>), 41.67 (NH-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>), 40.50. The product is soluble in common solvents such as chloroform, benzene, water, xylene or ethanol [6].

### 2.2. Synthesis of the Co(II) complex

The ligand (0.429 g, 2.0 mmole) was dissolved in 10 mL absolute ethanol in a 50 mL round bottom flask. A solution of 1 mmole of metal acetate Co(CH<sub>3</sub>COO)<sub>2</sub>·6H<sub>2</sub>O (0.249 g), in 5 mL absolute ethanol was added dropwise in a 15 min period with continuous stirring at room temperature. The reaction mixtures were then further stirred for 1–6 h at room temperature. The resulting precipitates were filtered and washed with absolute ether. The products were dissolved in chloroform and precipitated with n-hexane (1/5). The resulting crystals were filtered and dried at room temperature. The yield of complex was found to be 0.14 g (60.0%) for Co(II) [6].

The thin film of the compound was prepared by evaporating the solvent from a solution of the compound with subsequent drying of the film deposited on quartz substrate. The solution of the compound was homogenized for 2.5 hours and was rotated for homogeneous mixing. From the measured spectral curves, the average thickness of the film was determined using optical spectral curves of the compound [1–3, 7] and was found to be about 95 nm. The film was characterized by means of X-ray diffraction technique. But, no peak appeared in the X-ray pattern, which confirmed that the film had amorphous structure. The optical spectrum of the thin film was recorded by Shimadzu UV-12080 UV/VIS spectrophotometer at room temperature.

### 3. Results and discussion

The optical absorption is one of the most productive tools to understand the band gap of optical materials. The optical properties of a solid are governed by the interaction between the solid and the electric field of the electromagnetic wave. In the compound, a typical absorption edge can be broadly ascribed to either of the three processes: i) residual below-gap absorption; ii) Urbach tails; and iii) interband absorption. In the second process, the absorption edge depends exponentially on the photon energy according to the Urbach relation [8]. In crystalline materials the fundamental edge is directly related to the conduction and valence band, *i.e.*, direct and indirect band gaps, while in the case of amorphous materials a different type of optical absorption edge is observed. In these materials, parameter  $\alpha$  increases with the photon energy near the energy gap.

To determine optical band gap and optical constants of the compound, UV-VIS optical absorption study was made on the thin film. The spectral behavior of transmittance  $T(\lambda)$  and reflectance  $R(\lambda)$  of the film is shown in Fig. 1a, b. The optical absorption method was used to determine the optical band gap of the thin film, which is the most direct and simplest method. The fundamental absorption refers to band to band transitions and it manifests itself by a rapid rising in the absorption used to

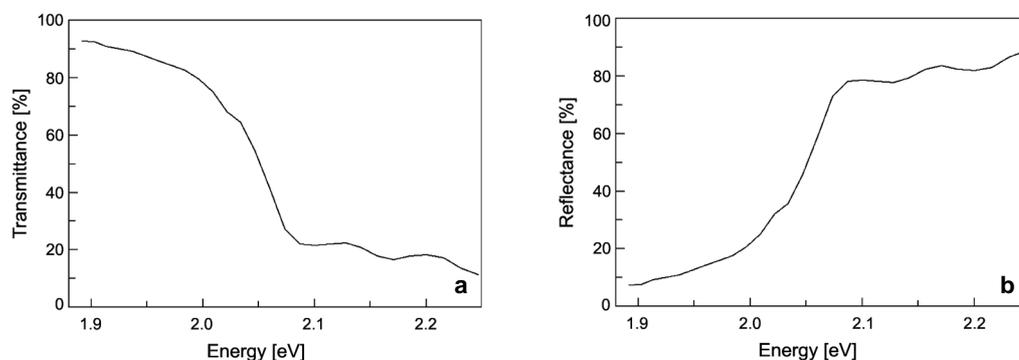


Fig. 1. Transmittance and reflectance spectra of the thin film.

determine the optical band gap. The absorption coefficient was obtained from the transmittance and reflectance spectra of the film using the relationship [9]

$$\alpha = -\frac{1}{t} \ln \left[ \frac{T}{(1-R)^2} \right] \quad (1)$$

where  $t$  is the thickness of the film. In the crystalline and amorphous materials, the optical absorption dependence of the photon energy is expressed by the following relationship [9, 10],

$$\alpha h\nu = A(h\nu - E_g)^m \quad (2)$$

where  $A$  is an energy-independent constant,  $E_g$  is the optical band gap and  $m$  is a constant which determines the type of optical transition ( $m = 1/2$  and  $3/2$  for direct allowed and forbidden transitions, respectively,  $m = 2$  and  $3$  for indirect allowed and forbidden transitions, respectively). The type of transition can be obtained finding the value of  $m$ . So, we obtained that the curve indicating the function of  $d(\ln\alpha)/d(h\nu) = f(h\nu)$  shows a change in its slope for a value of  $h\nu$ . The curve of  $\ln(\alpha h\nu)$  vs.  $\ln(h\nu - E_g)$  was plotted using the this value to determine  $m$  value and it was found about 2 from the slope of this curve, in which the electronic transition from the valence band to the conduction band is electrical dipole allowed, and electronic absorption is strong. Thus, a more precise value was obtained from the linear part of the  $(\alpha h\nu)^{1/2}$  vs.  $h\nu$ , as shown in Fig. 2 and its value is  $1.99 \pm 0.010$  eV.

In the exponential-edge region, the absorption coefficient is expressed by the so-called Urbach relationship [8]

$$\alpha(h\nu) = \alpha_o \exp\left(\frac{h\nu}{E_o}\right) \quad (3)$$

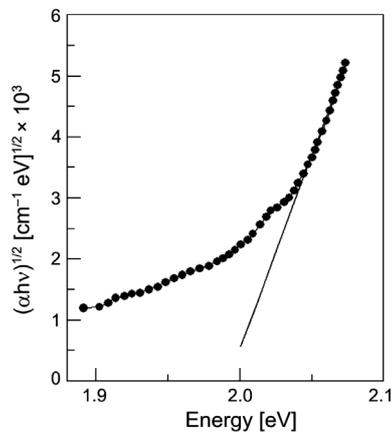


Fig. 2. The  $(\alpha h\nu)^{1/2}$  vs. energy plot of the thin film.

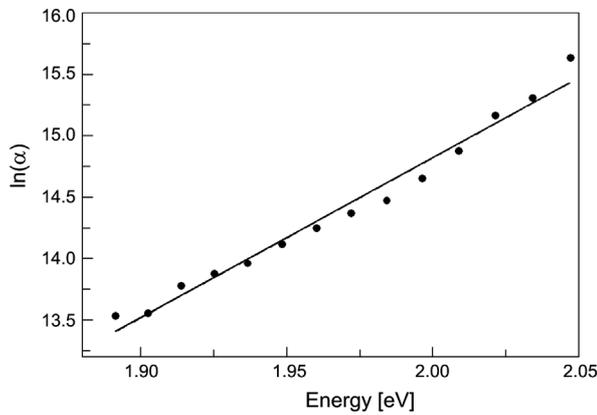


Fig. 3. Urbach plot of the thin film.

where  $\alpha_o$  is a constant and  $E_o$  is the Urbach energy, which characterizes the slope of the exponential edge region. We plotted the curve of  $\ln\alpha$  vs. photon energy, as shown in Fig. 3 and  $E_o$  value was calculated from the slope of this curve and was found to be  $76.85 \pm 0.01$  meV. Urbach energy  $E_o$  characterizes the slope of the exponential edge region and the inverse of the slope gives the width of the localized states associated with amorphous state in the band gap of the thin film. It is believed that the exponential dependence of  $\alpha$  on photon energy may arise from random fluctuations of the internal fields associated with the structural disorder in many amorphous materials. It is also evaluated that the exponential behavior of the absorption coefficient arises from the electronic transitions between localized states and their density falls off exponentially with photon energy. The width of localized states is the so-called Urbach energy [8]. The plot of  $\ln\alpha$  vs. photon energy is linear for the absorption region near the fundamental absorption edge. Thus, it is evaluated that the absorption coefficient near the fundamental absorption edge is exponentially dependent on the photon energy and obeys the Urbach rule. Urbach's absorption edge is formed in the region of photon energies below the forbidden band gap. The interaction between lattice vibrations and localized states in tail of the band gap of the compound has a significant effect on the optical properties of the thin film. In this disordered material, analog of  $E_g$  is the mobility gap [10].

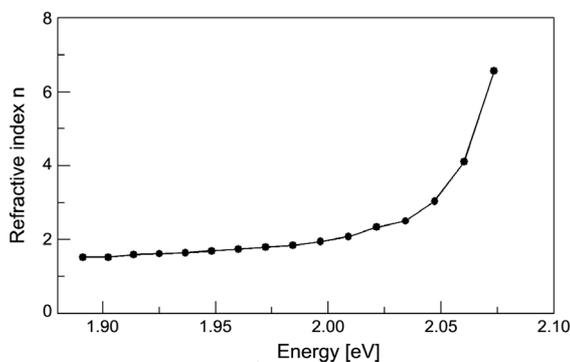


Fig. 4. Variation of refractive index with photon energy.

The refractive index plays an important role in the search for optical materials, being a significant factor in optical communication and in designing devices for spectral dispersion. Therefore, it is important to determine refractive index of the thin film. The refractive index of the film was calculated from transmittance and reflectance spectra [2, 3, 11]. The spectral curve of the refractive index is shown in Fig. 4. The refractive index of the film shows the normal dispersion up to about 2 eV and afterwards, the values of  $n$  increase with increasing photon energy.

#### 4. Conclusions

The optical band gap and the width of localized states of organic thin film were investigated. The studies on the thin film revealed that the nature of the electronic transition from valence band to conduction band is indirect transition. The exponential behavior of the absorption edge is attributed to the electronic transition in the localized states tailed off in the energy band gap. The optical band gap and width of localized states were respectively obtained as  $1.99 \pm 0.010$  eV and  $76.85 \pm 0.01$  meV.

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