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DIFFUSE REFLECTANCE OF CdO

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The diffuse reflectance of different samples of CdO prepared from $CdCO_3$ by firing at different temperatures from 400 and up to 1000°C was measured at room temperature in the wavelength range from 400 to 1500 nm. The energy gap of these different samples were then deduced as well as the position and number of the indirect transitions which were found to be dependent on the firing temperature. So we conclude that for firing temperatures less than 600°C Cd interstitials are present, while for firing temperatures greater than 700°C oxygen vacancies are the predominant. The more stoichiometric CdO may be prepared by firing $CdCO_3$ between 600 and 700°C, for which the energy gap is 2.3 eV with one indirect transition appearing at 1.2 eV gap.

1. Introduction

Cadmium oxide is a II—VI compound crystallizing in the NaCl structure, which exhibits nearly metallic *n*-type semiconductor with high conductivity due to its relatively large concentration of an ionized atomic defects.

The electrical properties of CdO along with its defect structure have been extensively investigated. Several studies have been done on CdO single crystal[1,2], compressed tablets[3,4] and on sputtered films [5-7]. However there are much reliability among the different results obtained, which may be due to the lack of control of the factors influencing the defect concentration during sample preparation. Anyhow, Hall coefficient of CdO specimens in the form of thin films, sintered powders[8] and single crystals[9] show that the carriers are mainly electrons generated by defects and have a concentration of 10^{18}—$10^{20}/cm^3$.

Nevertheless, there is no agreement on whether the principal defects are cadmium interstitials or oxygen vacancies, as for example Cimino[10] and Faivre[11] have investigated the defect structure of CdO by measuring the lattice parameters and concluded that cadmium interstitials are the important defects, which is in good agreement with the work done by Koffyberg[12]. Whereas Haal[13] deduced an oxygen vacancies through lattice diffusion studies on material equilibriated at 790°C and oxygen pressure of $1.62 \cdot 10^4$Pa. Lakshmanan[6] also found from the optical and electrical properties of CdO films that the principal defects are oxygen vacancies, while Engell[14] measured a cadmium excess in a sample sintered in air at 650°C.

Also by using optical measurements[8,15-17] an effective electron mass $m^* \approx$ $\approx 0.14\, m_e$, a direct band gap equal to 2.35 eV at room temperature and a possible indirect gap of $\approx$ 1.2 eV were given.

From an energy band calculation[18] it may be concluded that the direct gap is in the middle of the Brillouin zone between Γ_{15} and Γ_1. As Γ_{15} is not the maximum of valence band energies, the smallest gap of CdO should be less than 2.35 eV. Two indirect transitions between $\sum_3$ and Γ_1 (1.2 eV) and L_3 and Γ_1 (0.8 eV) were predicted.

The diffuse reflectance spectrum of the semiconducting powders is analogous to their transmition spectrum. A study of the tail of the absorption curve of semiconductor shows that it has nearly an exponential drop[19]. The onset of this drop has been taken and suggested as a more universal method of deducing the position of the absorption edge[20]. So Fosch[20] has taken the onset of the linear increase in diffuse reflectance R, i. e. the linear decrease in the absorption spectrum as a measure of the forbidden gap.

Tandon and Gupta[21] took the energy coordinate of the point on the low energy side of the absorption curve at which the linear increase in absorption starts as the value of the forbidden energy gap of semiconductors.

The aim of the present work is to find the effect of the method of preparing CdO, i. e. the firing temperature, on its gap width. The diffuse reflectance technique of the grounded powders was used to determine the dependence of both indirect, E_i, and the direct, E_g, energy gaps on the firing temperature.

The privilege of this method is that we are not in need to change the firing temperature during the experimental processes neither like thin film nor the electrical conductivity on the compressed powder or single crystal technique. Moreover, up to our knowledge, no previous results on the diffuse reflectance of CdO has been reported.

2. *Experimental*

It is well known that CdO may be prepared either by firing Cd metal or one of its salts in an oxygen atmosphere. Herewith, we prepared CdO by firing spec. pure $CdCO_3$ in an oxygen atmosphere for 6 hours. The reaction was followed by DTA measurements which showed that all temperatures above 350°C gave a complete transformation of $CdCO_3$ to CdO while below this temperature traces of carbonates still exsist, as shown clear from Fig. 1. So, $CdCO_3$ was fired between 400 and 1000°C in a decade of 100°C.

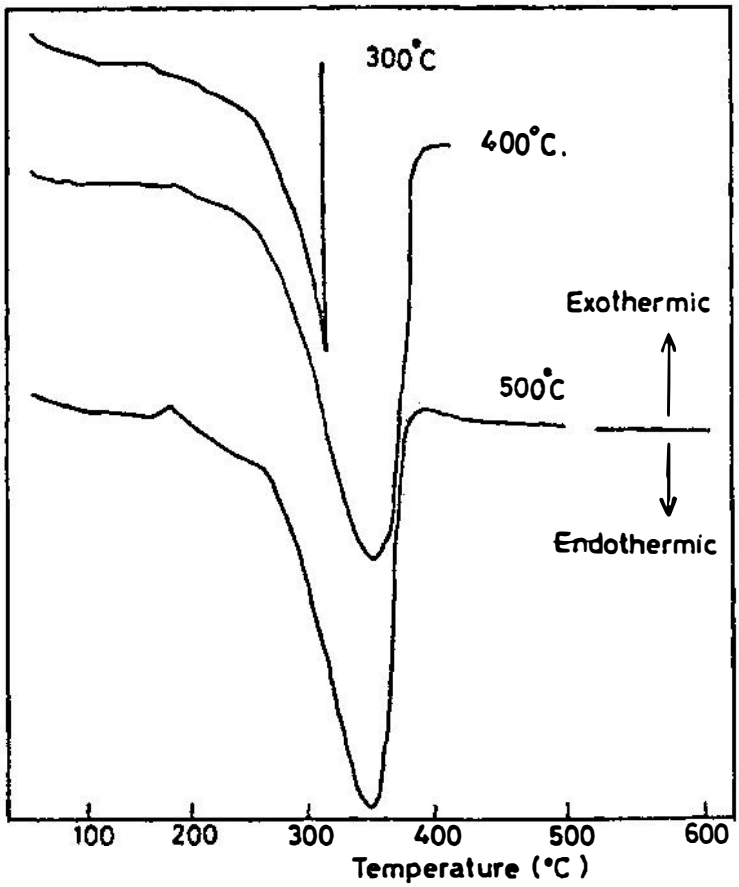

Fig. 1. Differential Thermal Analysis (DTA) of $CdCO_3$ at different temperatures in an oxygen atmosphere.

The fired samples were grounded carefully and sieved to have a unique particle size of 600 μm to avoid grain size effect and then compressed at the same low pressure using the hand press accompanied by the PMQ III spectrophotometer.

Diffuse reflectance measurements, in the range from 400 to 1500 nm, were carried out using the PMQ III spectrophotometer, which fitted with an integrated sphere diffuse reflectance attachment type RA3. The Kubelke-Munk remission function:

$$K/S = (1 - R)^2/2R$$

has been used as a measure of absorption by the powder samples[22,23], where K and S are the absorption and scattering coefficients, respectively.

The energy coordinate of the drop of the linear decrease in the absorption curve, i. e. in the high energy side, has been taken as a measure of the forbidden gap[20].

3. *Results and discussions*

The colour of the fired samples was found to be changed from light brown to light black with increasing the firing temperature as shown below:

Firing temperature (°C)	400	500	600	700	800	900	1000
Colour	Yellowish brown	Light brown	Brown	Dark brown	Greyish brown	Blackish brown	Light brown

Figs. 2a, 2b and 2c show the results of absorption variation (K/S) in relation to the photon energy ($h\nu$) for different samples obtained by firing $CdCO_3$ at 400, 500, 600, 700, 800, 900 and 1000°C. These results are reproducible, time independent at room temperature and do not change from one sample to another fired at the same temperature.

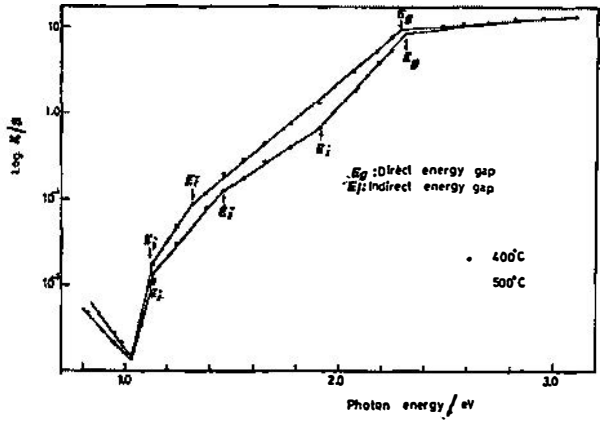

Fig. 2a. Absorption spectra of CdO obtained by firing $CdCO_3$ at 400 and 500°C.

These curves show that the energy gap, which is the highest point of the linear parts in the absorption curves varies with the firing temperature as shown in Fig. 3.

The spectra of CdO obtained by firing at 400°C shows some kinks in the linear portion of the absorption curve, which prove that this sample has three indirect transitions at 1.92 eV gap, 1.46 eV gap and 1.13 eV gap. Increasing the firing temperature to 500°C, two indirect transitions appear at 1.32 eV gap and at 1.13eV gap as shown in Fig. 2a. While for those samples obtained by firing at 600 and 700°C only one indirect transition was found to appear at 1.24 eV gap in each sample as shown in Fig. 2b.

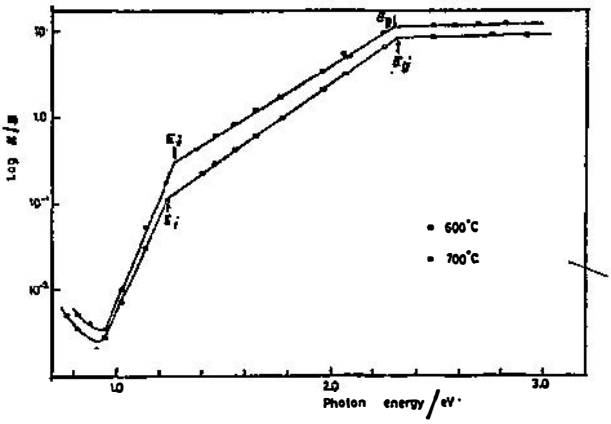

Fig. 2b. Absorption spectra of CdO obtained by firing $CdCO_3$ at 600 and 700°C

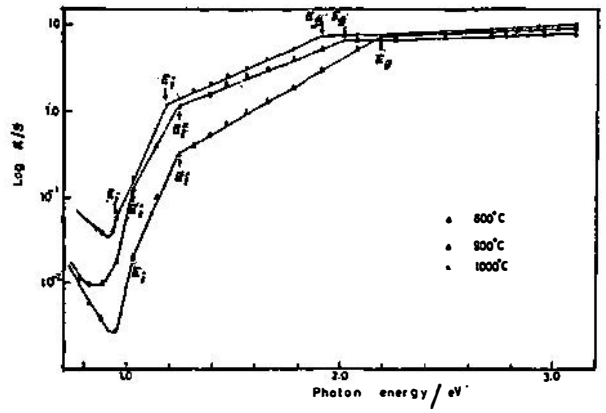

Fig. 2c. Absorption spectra of CdO obtained by firing $CdCO_3$ at 800, 900 and 1000°C.

Moreover, for further increase of the firing temperature to 800, 900 and 1000°C again two indirect transitions appear. These two transitions appear at 1.24 eV and 1.04 eV gap for the sample fired at 800°C. Increasing the temperature to 900°C the first transition appears also at 1.24 eV but the second one go to a value of 1.02 eV, while for the sample fired at 1000°C the transitions were found to appear at 1.18 eV and 0.94 eV gap as shown in Fig. 2c.

This behaviour may be explained by the fact that for low firing temperature, below 600°C, there are much possibility of the presence of Cd excess as interstitials, causing more than one indirect transition. While for high firing temperature, above 700°C, there are much possibility of loosing some oxygen atoms, causing an oxygen vacancies and again more than one indirect transition.

So far, our results are in fair agreement with the previous works namely an obtained energy gap $\approx$ 2.3 eV and indirect transition at 1.2 eV and possibly another one at a value less than 1.0 eV[4].

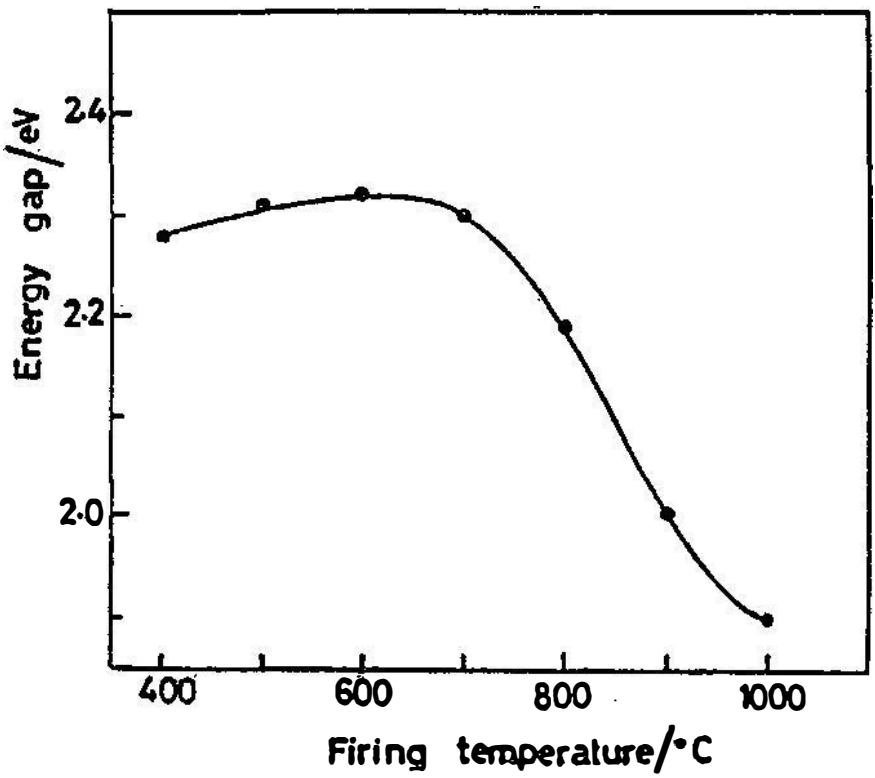

Fig. 3. Variation of energy gap with the firing temperature.

4. *Conclusions*

CdO can be prepared either by Cd interstitials or oxygen vacancies by controlling the firing temperature. Also from the energy gap dependence curve together with the indirect transition position the nearest stoichiometric CdO may be prepared between 600 and 700°C. Below and over this temperature limit non-stoichiometric CdO can be obtained.

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DIFUZNA REFLEKTACIJA KADMIJ OKSIDA (CdO)

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Difuzna reflektancija raznih uzoraka CdO formiranih pomoću žarenja $CdCO_3$ na različitim temperaturama od 400 do 1000°C, mjerila se kod sobne temperature u spektralnom području između 400 i 1500 nm. Iz tih mjerenja određivao se zabranjeni energetski procijep te broj i položaj indirektnih prijelaza, za koje je ustanovljeno da ovise o temperaturi žarenja. Analiza rezultata ukazuje na činjenicu da kod temperatura žarenja ispod 600°C u kadmij oksidu postoje intersticijski kadmijevi atomi, dok su iznad 700°C predominantne kisikove praznine. Najmanja odstupanja od stehiometrijskog odnosa komponenata u CdO se dobiju žarenjem kod temperatura u intervalu 600 do 700°C, za koje je određeno da energetski zabranjeni procijep iznosi 2,3 eV a indirektni zabranjeni pojas iznosi 1,2 eV.