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Diffuse Reflectance Measurements of Chromium Trioxide and Some of its Suboxides

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Diffuse reflectance / Chromium trioxide / Suboxides of chromium

The visible and near ultraviolet absorption spectra of CrO_{3-x} ($x = 0-1.5$) have been measured by diffuse reflectance method at room temperature. absorption peaks or maxima are interpreted as charge transfer. A common absorption maximum was obtained at ~4.8 eV.

The results indicated that the samples $CrO_{2.67}$ and $CrO_{2.41}$ are contaminated with Cr^{6+} and Cr^{4+} ions respectively. The band observed at 750 nm in $CrO_{1.98}$ spectrum was attributed to electron created from nonstoichiometry.

Introduction

The transition metal oxides form a groups of predominantly ionic solids which exhibit a wide range of optical and electrical properties. Many of these oxides have considerable use in electronic and magnetic devices. Little information is available in the literature on the energy band of 3d oxides such as CrO_3 [1–4]. This oxide tends to deviate from stoichiometry. The nonstoichiometry is associated with considerable modification of optical properties.

The present investigation is undertaken to make a systematic study of the diffuse reflectance spectra of stoichiometric CrO_3 and to compare the results with nonstoichiometry suboxides. For this reason, examination of the diffuse reflectance of CrO_3, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.51}$, $CrO_{2.46}$, $CrO_{2.41}$, $CrO_{1.98}$ and $CrO_{1.5}$ are carried out to derive more information about the effect of interactions in crystals of these oxides on the spectrum. This paper can be considered as continuation of previously measured physico-chemical properties of CrO_3 and its suboxides [5–7].

Table 1.

Solid	Preparation Temp. °C	Composition of the obtained solid
CrO_3	230	$CrO_{2.88}$
CrO_3	280	$CrO_{2.67}$
CrO_3	320	$CrO_{2.51}$
CrO_3	340	$CrO_{2.46}$
CrO_3	360	$CrO_{2.41}$
CrO_3	400	$CrO_{1.98}$
CrO_3	1000	$CrO_{1.50}$

Experimental

Different samples of CrO_3 were prepared as given in Table 1 at 230–1000 °C in a closed system [8]. More details concerning the method of preparation, chemical and X-ray analyses were described in previous publications [5, 9]. The samples were sieved through the 200 μm mesh to give the same average particle size.

The optical measurements were carried out using a Shimadzu double beam monochromator recording spectrophotometer model UV-360 (204–23300). Using an integrating sphere attachment special for powder samples. The spectrum was recorded from 200–800 nm against a reference path USP MgO. The first derivative was checked to detect the exact position of the absorption edge [10].

Results and discussion

The reflectivity change against the wavelength as recorded from the spectrophotometer for CrO_3, $CrO_{2.88}$, $CrO_{2.67}$, $CrO_{2.46}$, $CrO_{2.41}$, $CrO_{1.98}$ and $CrO_{1.50}$ are represented in Fig. 1. Table 2 gives the position of the bands [in eV]. An examination of the spectra for the different samples shows a common absorption maximum at $\sim(4.86 \pm 0.08)$ eV. It can be mentioned here that the position of this peak is independent of the sample composition and structure while its intensity decreases steadily with increasing oxygen deficiency. Szabó [11] showed that, Cr^{6+} exhibits an absorption peak at 4.7 eV and identified it with the ${}^1A_1 \rightarrow {}^1T_2$ transition. Darrie [12] noted that the value amounting to 4.5 eV was corresponding to ${}^3t_2 \rightarrow 2\,e$ transition for CrO_3.

Different authors [1, 2, 4, 13, 14] interpreted the position of absorption peak at 4.1–5 eV as due to charge transfer ${}^4A_{2g}$ $(t_{2g}^3 \xrightarrow{20D_q} {}^4T_{1g}(t_{2g}e_g^2)$. For the samples of intermediate composition between CrO_3–Cr_2O_3, this common

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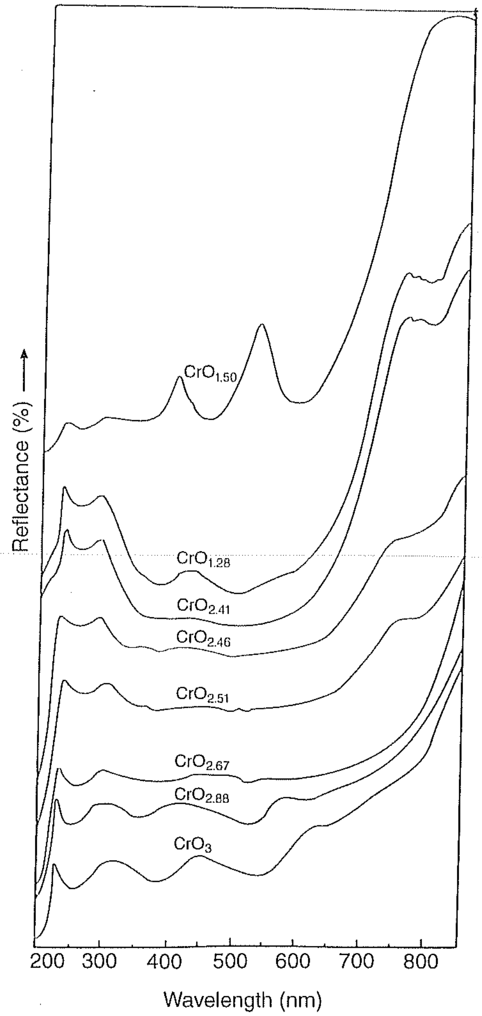

Fig. 1. Diffuse reflectance of chromium trioxide and some of its suboxides.

absorption peak was not previously reported in the literature. It is safe to concluded that the presence of this peak in the spectra of all samples may be due to the fact that the above charge transfer is predominant although these samples have different O/Cr ratio and structure [9]. The pronounced effect of the lattice is the decrease in the intensity of this band with reduction of chromium ion valency from +6 to +3 [2].

Absorption spectra in the region lower than 4.0 eV depend, to a certain extent, on crystal structure of the investigated samples and/or different oxy-

Table 2. The absorption bands of chromium trioxide and some of its suboxides (eV).

CrO_3	$CrO_{2.88}$	$CrO_{2.67}$	$CrO_{2.51}$	$CrO_{2.46}$	$CrO_{2.41}$	$CrO_{1.98}$	$CrO_{1.50}$
1.57	1.60	1.51	1.53	1.53	1.51	1.51	1.65
					1.55	1.56	
		1.71	1.75	1.79	1.76	1.78	
2.25	2.29					2.48	2.10
3.14	3.39					3.30	2.68
4.72	4.86	4.86	4.88	4.77	4.77	4.77	4.94

gen deficiency and crystal field splittings which may lead to a variable interband absorption spectrum observed in Fig. 1. According to the X-ray diffraction patterns and infrared spectra [9], the oxidation state of chromium ion present in these samples are as following:

1. CrO_3 and $CrO_{2.88}$ "Cr^{6+}" (orthorhombic system)
2. $CrO_{2.67}$, $Cr_{2.51}$, $CrO_{2.46}$ and $CrO_{2.41}$ "Cr^{5+}" (orthorhombic system)
3. $CrO_{1.98}$ "Cr^{4+}" (tetragonal)
4. $CrO_{1.5}$ "Cr^{3+}" (hexagonal).

These measurements gave no evidence of mixed valences in the above samples [9].

Going parallel to the above illustration, it can be observed that the reflectance spectra of CrO_3 and $CrO_{2.88}$ show Cr^{6+} charge transfer bands at 3.14, 2.25 eV and 3.39, 2.29 eV respectively.

Different authors [1, 11, 12] obtained the value amounting ~3.3 eV for the $t_1 \rightarrow 2e$ or $^1A_1 \rightarrow {}^1T_2$ transition for Cr^{6+}. Also, Van Arkel [15] estimated the value of 3.14 eV for the gap width of CrO_3 by the electrical conductivity method. Thus, it is expected that the absorption peak at 3.14 and 3.99 eV for CrO_3 and $CrO_{2.88}$, respectively, correspond to the transition of an electron of the valence band to the conduction band of Cr^{6+}. The variation of the position of this peak for CrO_3 and $CrO_{2.88}$ may be correlated to the variation in oxygen deficiency as they have the same crystal structure (orthorhombic). The same result was reached by Khilla *et al.* [16] for WO_3 oxide. Also Vernon [17] *et al.* studied the optical spectra of 25 transition metal oxides. They found that the transition energies of the maxima varied logarithmically with the carrier concentration due to lattice defects.

The second absorption peak appearing in the spectra of CrO_3 and $CrO_{2.88}$ lies at 2.25 and 2.29 eV respectively. Szabó [11] interpreted the peak at 2.7 eV as due to a tetrahedral strong field (Cr^{6+} to $^1T_1$) transition from the $^1A_1$ ground state in Cr^{6+}. It is clear that this transition is independent of oxygen deficiency.

Spectra of CrO_3 and $CrO_{2.88}$ show an absorption maximum at 1.57 and 1.60 eV, respectively, which may be compared with that obtained by Ellison [1] at 1.7 eV. He correlated this value to ground electronic term (^4P) sepa-

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In case of the second group, and from the spectra of CrO$_{2.67}$, CrO$_{2.51}$, CrO$_{2.46}$ and CrO$_{2.41}$ several conclusions can be drawn. The absorption peaks at 3.14 and 2.25 eV of CrO$_3$ appear as very weak and broad in the composition CrO$_{2.67}$. This may be explained by the contamination of these samples with Cr^{6+} which cannot be detected by X-ray diffraction or infrared studies. These peaks disappear in other samples; this indicates that they are totally free from Cr^{6+} ions.

The plateau or peak observed in the lower absorption maximum for the samples CrO$_{2.51}$, CrO$_{2.46}$ and CrO$_{2.41}$ (Fig. 1), can be explained by assuming that the distortion in symmetry of these samples (Cr^{5+}) is enough to cause this splitting [11]. This distortion may be created from the oxygen deficiency. Darrie [12] stated that at all stages of the decomposition of CrO$_3$, the amount of oxygen lost is directly proportional to the number of electrons transfered to chromium. Thus, the splitting of absorption maxima observed in the spectra of the above samples (CrO$_{2.51-2.41}$) may be attributed essentially to the increase of electron due to nonstoichiometry.

The absorption spectrum of CrO$_{1.98}$ exhibits two very weak broad absorption peaks at 3.26 and 2.43 eV, two absorption maxima at 1.78 and 1.51 eV and one absorption peak at 1.56 eV. Chase [3] obtained the absorption bands at 1.5, 1.7, 2.7 and 3.1 eV for CrO$_2$. These values are nearly the same as those obtained for CrO$_{1.98}$ and are attributed to the presence of Cr^{+4}.

Samples of CrO$_{1.50}$ show absorption peaks at 2.68, 2.10 eV, and maximum absorption at 1.65 eV. Poole [18, 19] has already interpreted some energy features of the level diagram of Cr^{3+} in an octahedral and in an octahedral plus a trigonal crystal field environment. Companion [14] stated that Cr^{3+} give absorption peak at 2.6 eV which correspond to the $^4A_{2g}-^4T_{1g}$ (t^2 e) transition. The energy levels at 2.10 and 1.65 eV are attributed to the $^2A_2 \rightarrow {}^4T_2$ and $^4A_{2g} \rightarrow {}^4T_{2g}$, respectively.

Different authors [1–4] stated that, CrO$_3$ and Cr$_2$O$_3$ are the more stable forms of chromium oxides, while suboxides represent the impure oxides. As mentioned before, the spectra of intermediate samples contain knees, plateaus or peaks, at lower energies (Fig. 1). They represent the effect of lattice defects, and disappear in the stable samples (CrO$_3$ and Cr$_2$O$_3$).

In conclusion, the qualitative features of the shapes of optical absorption spectra of CrO$_3$ and some of its suboxides may be used as measure for the departure from stoichiometry.

Acknowledgment

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