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CADMIUM METAVANADATE FORMATION. PART II. QUANTITATIVE X-RAY DIFFRACTION, SCANNING ELECTRON MICROSCOPY AND EDS STUDIES

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ABSTRACT

The synthesis of α-CdV_2O_6 at room temperature from an equimolar CdO–V_2O_5 mixture in a water-saturated atmosphere is studied.

A global quantitative evaluation of the CdO–V_2O_5 reaction is carried out with the aid of quantitative X-ray diffraction and EDS. The morphological evolution of a mixture of both oxides and the $\alpha \rightarrow \beta$ morphological transformation of CdV_2O_6 is studied by scanning electron microscopy.

INTRODUCTION

In the first part of this work the evolution of the CdO–V_2O_5 system (1 : 1) is studied in a water-saturated atmosphere at room temperature. X-Ray diffraction, IR spectroscopy and TG techniques have allowed us to establish the formation of α-CdV_2O_6 and its later partial transformation into the β form (high temperature allotropic form), so allowing us to propose a reaction mechanism based on the acid–base reactivity of V_2O_5 and CdO, greatly increased by the humidity.

In the second part of this work, using scanning electron microscopy (SEM), the morphological evolution of a mixture of both oxides during the reaction process, and the later transformation of α-CdV_2O_6 into β-CdV_2O_6 is studied.

A global quantitative evaluation of the CdO–V_2O_5 reaction has been carried out by quantitative X-ray diffraction and EDS (energy dispersive spectrometry).

EXPERIMENTAL

Sample preparation

The samples studied were prepared from an equimolar mixture of crystalline V_2O_5 (Merck, AR > 99%) and crystalline CdO (Riedel de Häen AG, heated to 400°C for 2 h). The grain size of these reactives was less than 50 μm. Such mixtures were maintained at room temperature in a water-saturated atmosphere for different periods of time: $7\frac{1}{2}$ h, 1, 3, 6, 12 and 134 days.

Apparatus

X-ray powder diffraction

A Siemens diffractometer model D-500 and a graphite monochromator K 805, generating Cu $K\alpha$, radiation (1.5405 Å) were used.

Scanning electron microscopy

A Jeol JST9 35C instrument was used with an energy dispersive spectrometer (Kevex 7077). The samples were metallized with gold (200 Å) by sputtering. The semiquantitative microanalyses were made at 20 kV and a reference current of 300 μA.

RESULTS AND DISCUSSION

Quantitative analysis by X-ray diffraction (XRD)

Among the five most used methods for the quantitative analysis by XRD [1–8] we have chosen the internal standard method. We have selected the CdO phase, because as it can be seen in the X-ray diffractogram (Fig. 1) corresponding to a sample in which the reaction has begun, the most intense and unoverlapped line is at 2.71 Å, corresponding to CdO (111) plane where $I/I_1 = 100$. The calcite mineral phase was chosen as the internal standard, because this compound possesses the properties demanded by the N.B.S.: the most intense line of this phase (3.035 Å, (104) plane), appears in an angular zone near the analytical line and does not interfere with any other. Calcite was added to synthetic mixtures at 25 wt.%; V_2O_5 was used as the matrix.

Calibration curve

Twelve synthetic mixtures of CdO, V_2O_5 and $CaCO_3$ were prepared. Table 1 shows the weight of CdO (%), the intensities of the analytical (I_a) and internal standard (I_s) lines and the ratios between them. The values are the average of three measurements.

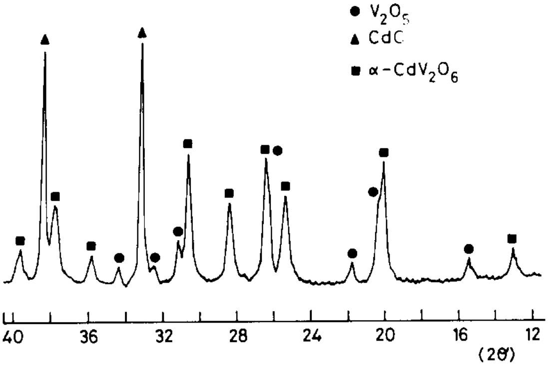

Fig. 1. X-ray diffraction pattern of CdO–V_2O_5 mixture treated in a water-saturated atmosphere at 25° C for 3 days.

TABLE 1

X-ray diffraction calibration data

CdO (%)	I_a (cm)	I_s (cm)	I_a/I_s
0	0	4.0	0
4	1.4	4.0	0.35
8	2.6	4.6	0.56
17	3.3	5.0	0.66
33	6.0	3.6	1.7
42	7.8	4.2	1.9
50	9.0	4.4	2.0
58	11.2	4.2	2.7
67	10.2	3.7	2.8
75	13.3	3.8	3.9
92	13.0	3.3	3.9
100	15.2	4.6	4.6

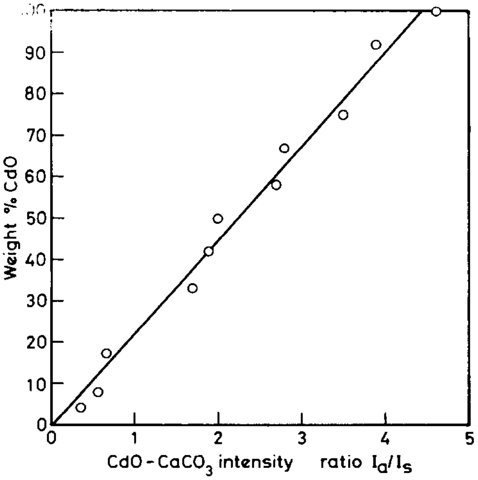

Fig. 2. Calibration curve for CdO analysis using calcite as internal standard.

TABLE 2

Effect of treatment time on the intensities of analytical (CdO) and standard ($CaCO_3$) lines and their ratios

Sample $CdO-V_2O_5$	I_a (cm)	I_s (cm)	I_a/I_s
0 h	7.4	4.1	1.8
$7\frac{1}{2}$ h	5.4	3.7	1.5
1 day	3.1	3.5	0.89
3 days	2.05	3.7	0.55
6 days	0.9	3.8	0.24
12 days	0	3.6	0
134 days	0	3.7	0

Figure 2 shows that the calibration curve is linear and passes through the origin, according to the equation

$$W_a = K\frac{I_a}{I_s}$$

given by Alexander and Klug in 1948 [7]. The standard deviation was 13%.

Quantitative analysis of $CdO-V_2O_5$ (1 : 1) mixtures

Table 2 shows the values of the intensities of analytical (CdO) and standard ($CaCO_3$) lines, and their ratios. From these values and according to the calibration curve the percentage in weight of CdO can be calculated for all samples. The percentage of V_2O_5 and CdV_2O_6 has been calculated from the experimental data for CdO (Table 3); the first by the stoichiometry of the mixture and the second by difference.

Scanning electron microscopy (SEM)

Studies made by SEM have allowed us to establish the morphology of α-CdV_2O_6 obtained at room temperature, and its later transformation into β-CdV_2O_6. As we know, no morphological data on these compounds have been given.

TABLE 3

Effect of treatment time on the composition of the reaction mixture

Sample (%)	Treatment time					
	0 h	$7\frac{1}{2}$ h	1 day	3 days	6 days	12 days
CdO	41	33	20	12	6	0
V_2O_5	59	47	29	17	8	0
CdV_2O_6	0	20	51	71	86	100

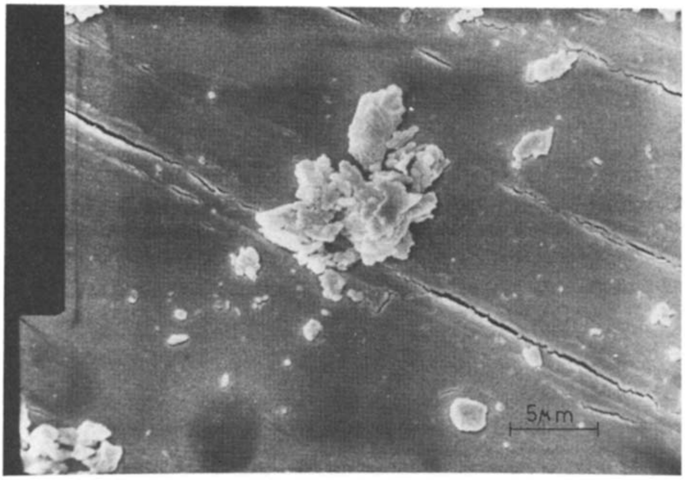

Fig. 3. Scanning electron micrograph of V_2O_5.

The morphologies of V_2O_5 and CdO can be observed in Figs. 3 and 4, respectively. V_2O_5 (Fig. 3) appears in stratified layers of different sizes, due to the breakage of crystals during grinding. CdO (Fig. 4) appears as spherical crystals smaller than those of V_2O_5. α-CdV_2O_6 and β-CdV_2O_6 are clearly distinguished due to the different aciculate morphologies, as can be seen in the A and B zones of Fig. 5.

Semiquantitative analysis by EDS

The morphological study of the different phases present in the studied reaction has allowed us to complete the data published in the first part of

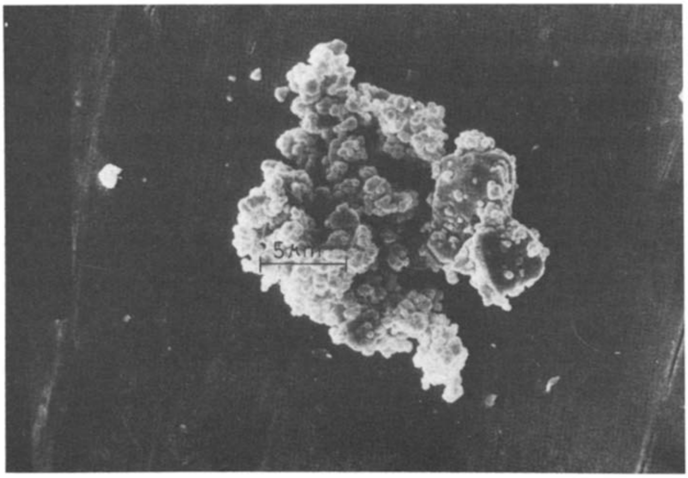

Fig. 4. Scanning electron micrograph of CdO.

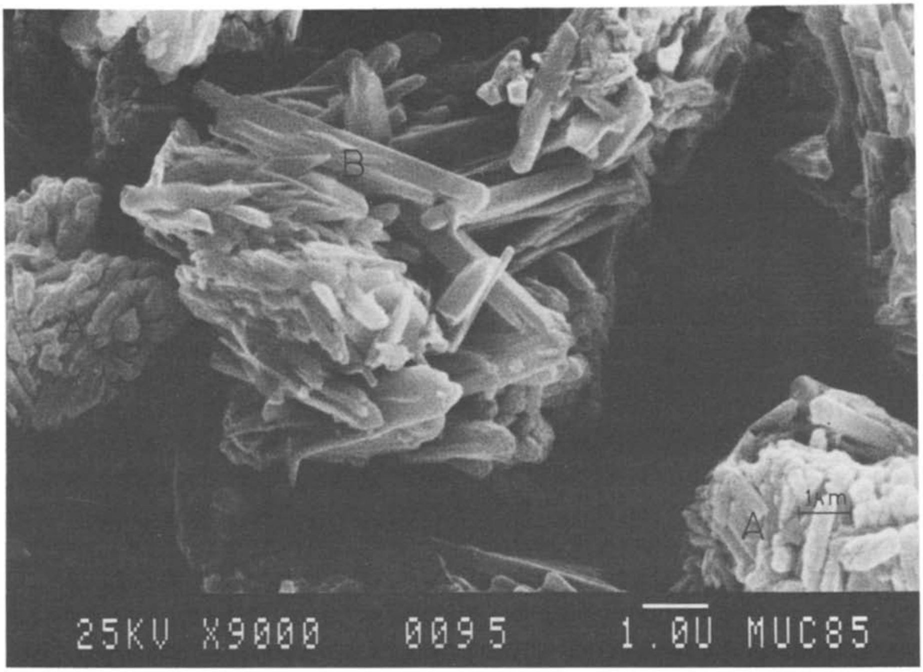

Fig. 5. Scanning electron micrograph of α- and β-CdV_2O_6 mixture: A zone, morphology of α form; B zone, morphology of β form.

the work. Thus in Fig. 6, corresponding to a mixture treated for 7½ h in humidity, containing 20% α-CdV_2O_6 (Table 3), three different morphologies (A, B and C zones) can be distinguished. In the A zone small aggregates of aciculate morphology appear to be growing, corresponding to α-CdV_2O_6; the EDS point analysis of this zone gives 100% CdV_2O_6 phase. In the B zone, stratified layers can be seen, similar to those of Fig. 3, due to the unreacted V_2O_5 phase; the EDS point analysis gives 73% V_2O_5 and 27% CdO. In the C zone, spherical crystals, similar to those shown in Fig. 4, are observed corresponding to the CdO phase; the EDS analysis detects 68% CdO and 32% V_2O_5.

Due to the layered texture of V_2O_5 with an interlayer distance of 4.4 Å, it seems possible to affirm that such an oxide is the support for α-CdV_2O_6 formation. Therefore the CdO molecules are intercalated between its layers in the same form as the H_2O molecules.

After one day of reaction in a humid atmosphere, 51% α-CdV_2O_6 is present (Table 3). As can be observed in Fig. 7 (zone A), the number of aciculate aggregates has increased, as has their size. The EDS analysis of this zone gives 100% CdV_2O_6.

After 12 days, the reaction has finished and α-CdV_2O_6 is the only phase in the system (Table 3). Its micrograph (Fig. 8) shows a unique morphology. The EDS analysis gives 100% CdV_2O_6 in all zones.

If the contact of α-CdV_2O_6 with the humid atmosphere is prolonged for 134 days at room temperature, the presence of β-CdV_2O_6 (allotropic variety of high temperature) is observed by XRD. In Fig. 5 the two different textures of the aciculate morphology of CdV_2O_6 can be seen. In the A zone,

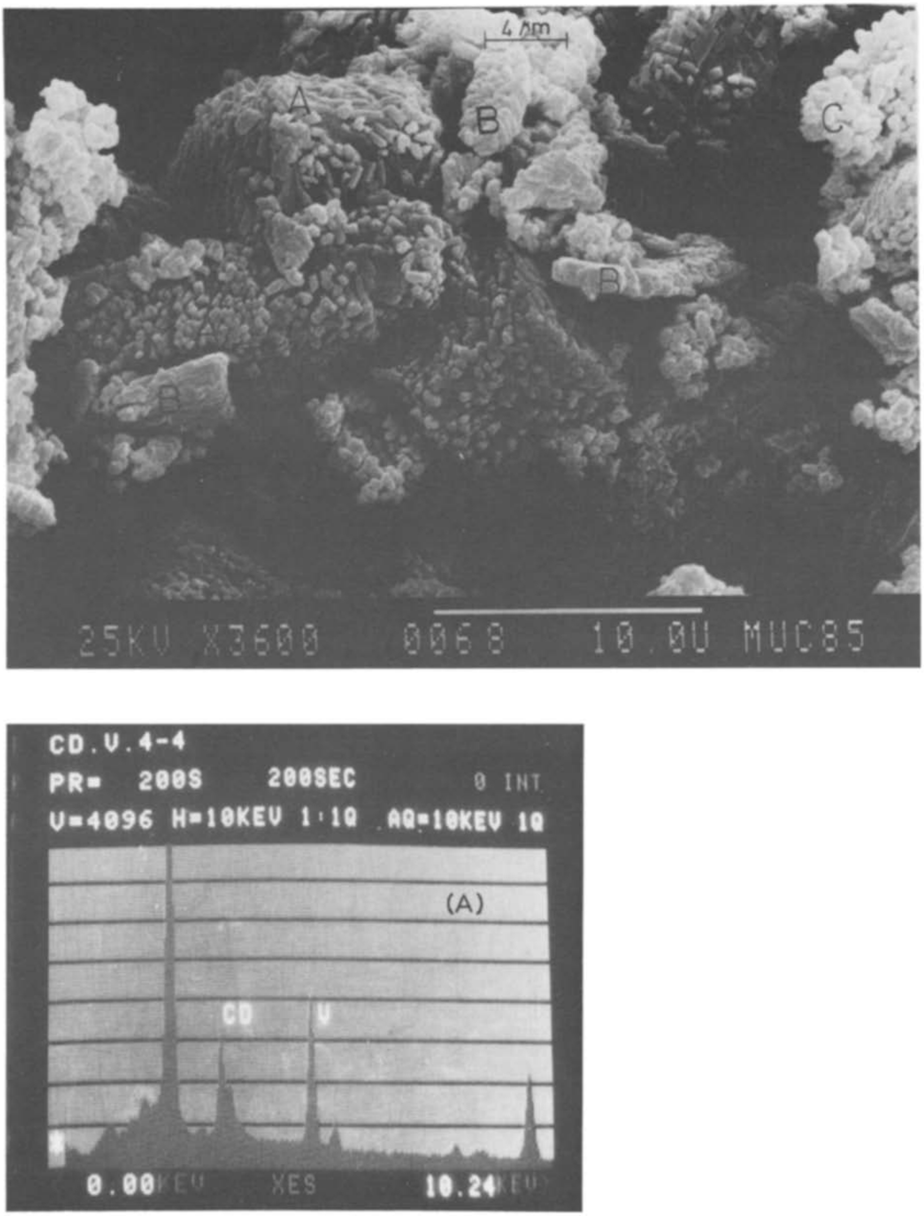

Fig. 6. Scanning electron micrograph and EDS of CdO–V_2O_5 mixture treated for $7\frac{1}{2}$ h in a humidity saturated atmosphere: A zone, morphology of α-CdV_2O_6; B zone, morphology of V_2O_5; C zone, morphology of CdO.

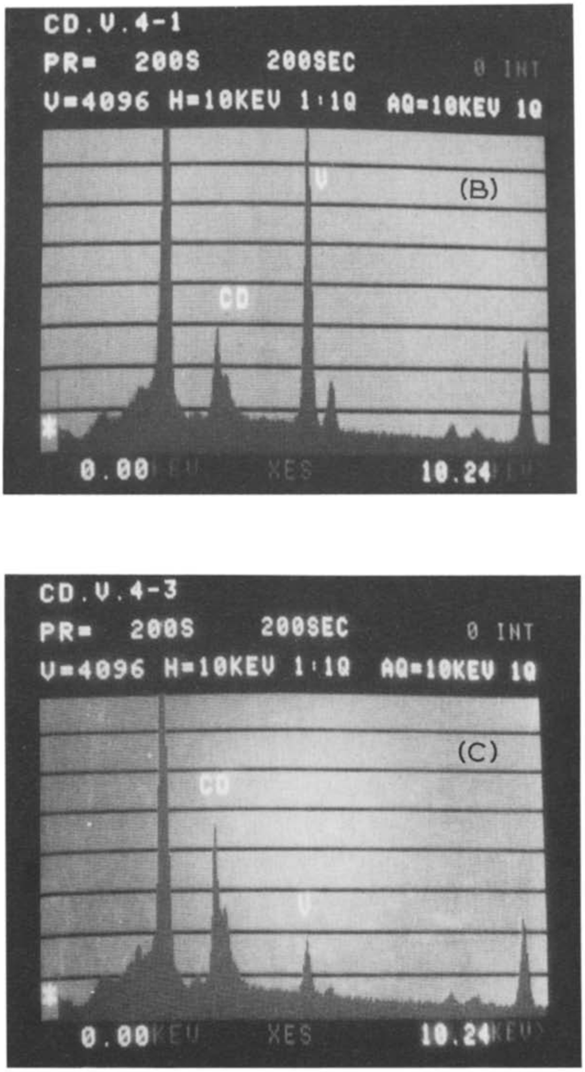

Fig. 6 (continued).

there are crystalline aggregates similar to those observed for the α form in previous samples. In the B zone aciculate aggregates are larger in size and more compact than the α ones, corresponding to the β-CdV_2O_6 phase. Thus, the α-CdV_2O_6 has undergone an allotropic transformation to the β form.

According to the structural studies on two α, β allotropic varieties of

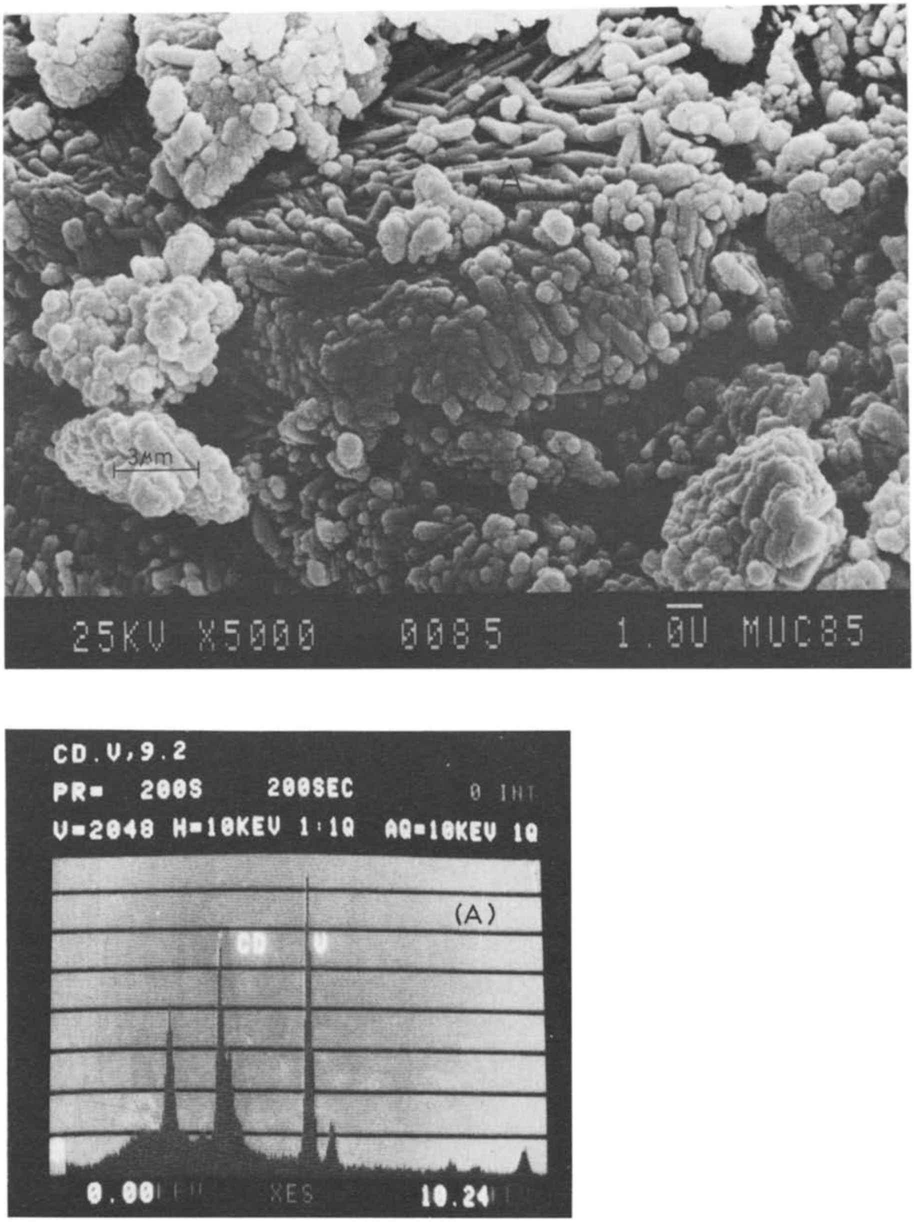

Fig. 7. Scanning electron micrograph and EDS of CdO–V_2O_5 mixture treated for 1 day in a water-saturated atmosphere: A zone, morphology of α-CdV_2O_6.

CdV_2O_6 made by Bouloux et al. [9,10], both metavanadates present a monoclinic structure with the following parameters:

α-CdV_2O_6: $a = 9.794$ Å; $b = 3.616$ Å; $c = 7.018$ Å; $\beta = 103.8°$

β-CdV_2O_6: $a = 9.359$ Å, $b = 3.568$ Å; $c = 6.980$ Å; $\beta = 112°$

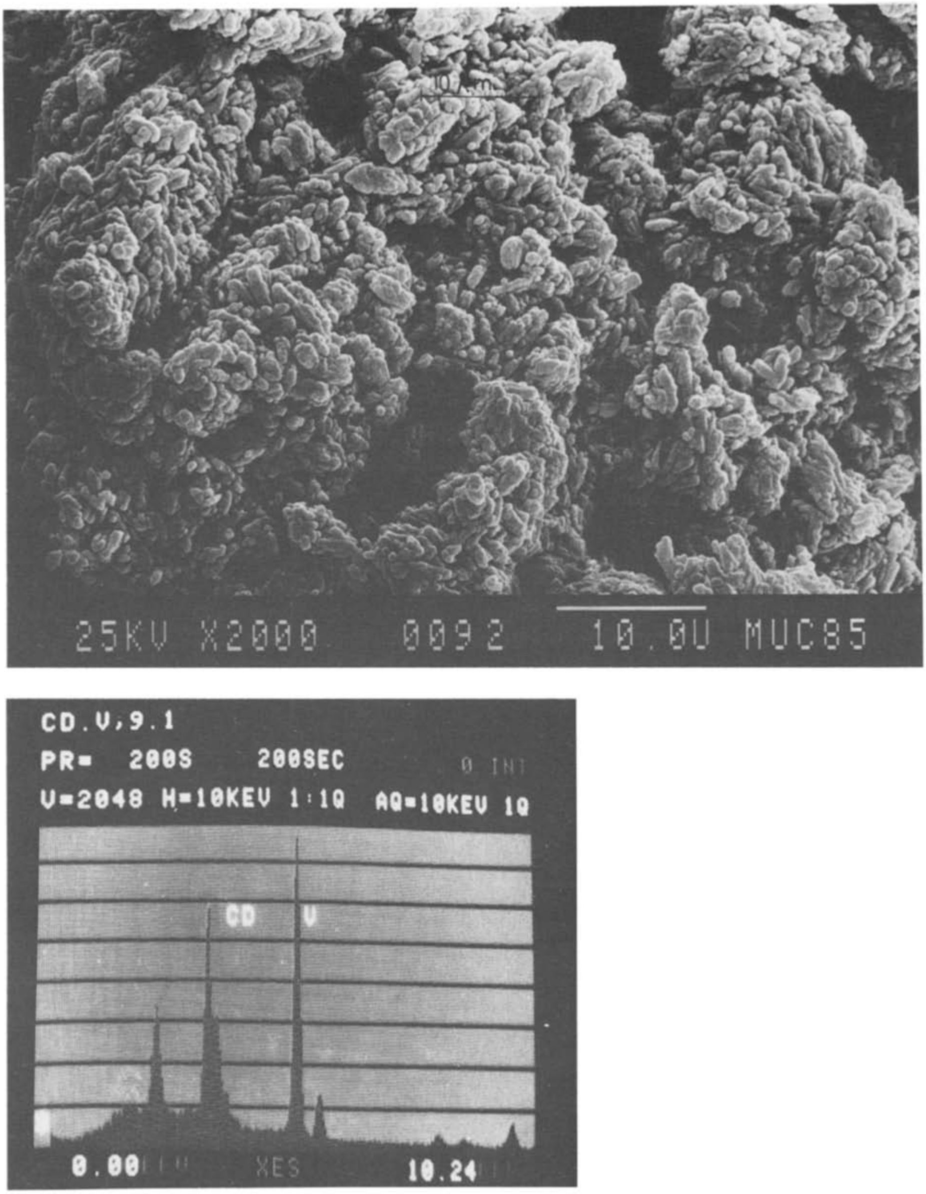

Fig. 8. Scanning electron micrograph and EDS of α-CdV_2O_6.

The β parameters are smaller than the α ones; therefore the structure of β-CdV_2O_6 is more compact, according to the morphologies observed in Fig. 5.

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