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Note

IR, X-RAY DIFFRACTION AND THERMAL STUDIES OF CADMIUM ZIRCONYL OXALATE HYDRATE

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The technological importance of various ABO_3 type mixed oxides attracted the attention of chemists and ceramists to prepare them by simpler methods with high purity. The method of preparation and calcination temperature affect the properties of materials considerably [1,2]. Mixed oxides in pure and homogeneous form can be obtained from thermal decomposition of precursor oxalates [3]. Zirconium is reported to form anionic oxalato zirconates of bivalent metal cations [4]. Hence, the present work is undertaken to prepare, characterize and study the thermal decomposition of cadmium zirconyl oxalate pentahydrate (CdZrOX) whereby a mixed oxide is obtained as end product.

EXPERIMENTAL

All the reagents used in the present study were either E Merck proanalysi or BDH AnalaR grade. The zirconium oxychloride octahydrate was of Fluka AG, Switzerland. The cadmium zirconyl oxalate was prepared by taking equimolar (0.5 M) aqueous solutions of cadmium nitrate and zirconium oxychloride which were slowly added to (1.0 M) warm oxalic acid solution. The precipitate appeared slowly and settled after being kept for 2 h at room temperature. The well settled precipitate was filtered and washed with distilled water containing a small amount of oxalic acid and then with acetone; the product was dried at room temperature. Such a sample was subjected to chemical analysis for various constituents and the data are: Cd, 23.20; ZrO, 22.0; C_2O_4, 36.35; H_2O, 18.5%, whereas the calculated values for $CdZrO(C_2O_4)_2 \cdot 5\,H_2O$ are: Cd, 23.15; ZrO, 22.08; C_2O_4, 36.24 and H_2O, 18.54%. These data show that there is no noticeable deviation for CdZrOX with the composition $CdZrO(C_2O_4)_2 \cdot 5\,H_2O$. The X-ray powder diffraction studies indicate that CdZrOX is a crystalline compound and some of the *d*-values are reported in Table 1. The thermogravimetry was carried out using a Stanton thermobalance (HT model) with 50—100 mg samples in platinum crucibles at a heating rate of 7°C min^{-1}. The differential thermal analysis were carried out by employing a Fisher differential thermalyzer Model 260 P, fitted with a voltage stabilizer, controller, amplifier and atomatic recorder. 100—150 mg samples were taken in quartz crucibles and the heating rate was 10°C min^{-1}. IR

TABLE 1

IR data of CdZrOX		X-Ray data of CdZrOX d-values (Å)
Band position (cm^{-1})	Assignment	
3400	νOH of H_2O	6.530 [b]
1680	νa(C=O)	5.630 [a]
1420	νa(C—O) + ν(C—C)	5.270 [b]
1390, 1360, 1300	νs(C—O) + δ(O—C=O)	4.434
900	ν(C—O) + ν(Zr—O) + δ(O—C=O)	3.765 [c] 3.319
810	δ(O—C=O) + (MO)	2.935
610	ν(M—O) + δ(ring) + δ(O—C=O)	2.821 [c] 2.466 2.222 2.098 [c]

a = Strongest; b = very strong; c = strong.

spectra were recorded on a Beckman IR-20 double beam instrument in the range 4000—250 cm^{-1} with samples in KBr pellets. The X-ray powder diffraction studies were carried out on 'Siemens' and 'Philips' diffractometers using CoK_a and CuK_a radiation, respectively.

RESULTS AND DISCUSSION

The results of the IR studies (Fig. 1a) of cadmium zirconyl oxalate pentahydrate (CdZrOX) are summarized in Table 1 and the assignments to various bands are made based on the available data in the literature [5—9].

The acetone-washed sample contains 5 moles H_2O mole^{-1} CdZrOx. Thermal analysis of such a sample shows that its decomposition is simple in comparison to the previous studies made on other oxalato zirconates [10—12] and proceeds through two stages, the first being the dehydration and the second the decomposition of the oxalate.

Dehydration

The dehydration takes place between room temperature (RT) and 190°C with the loss of all the water. This stage is observed clearly in DTA and TG (Fig. 2). The peak corresponding to dehydration in DTA is around 150°C. However, the observed weight loss in TG is 16.50%, compared with the calculated value of 18.5%. This indicates that a small amount of water is still held in the solid.

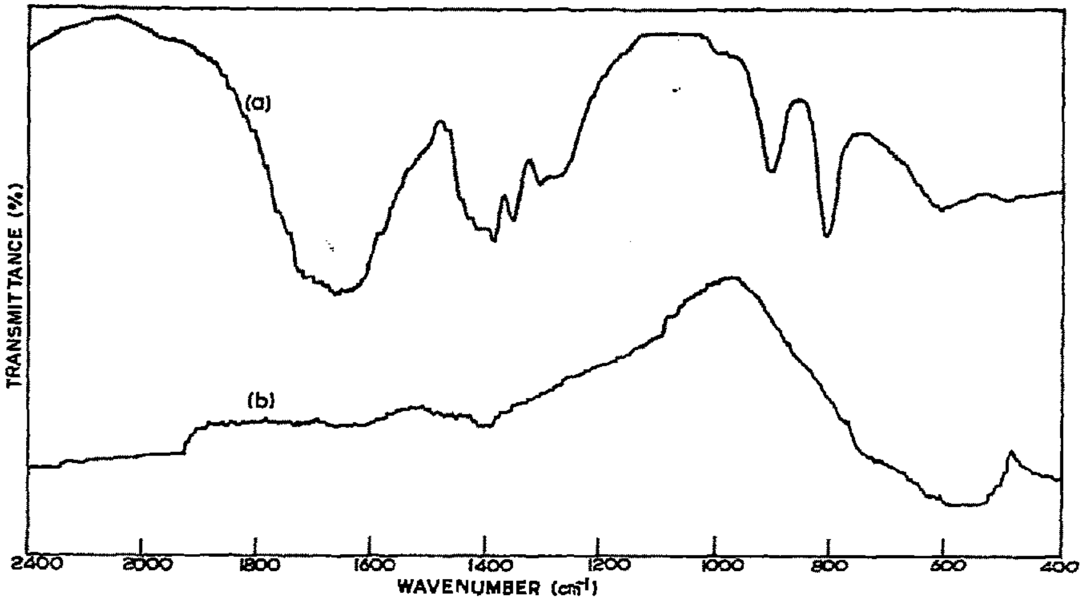

Fig. 1. IR spectra of (a) CdZrOx and (b) end product.

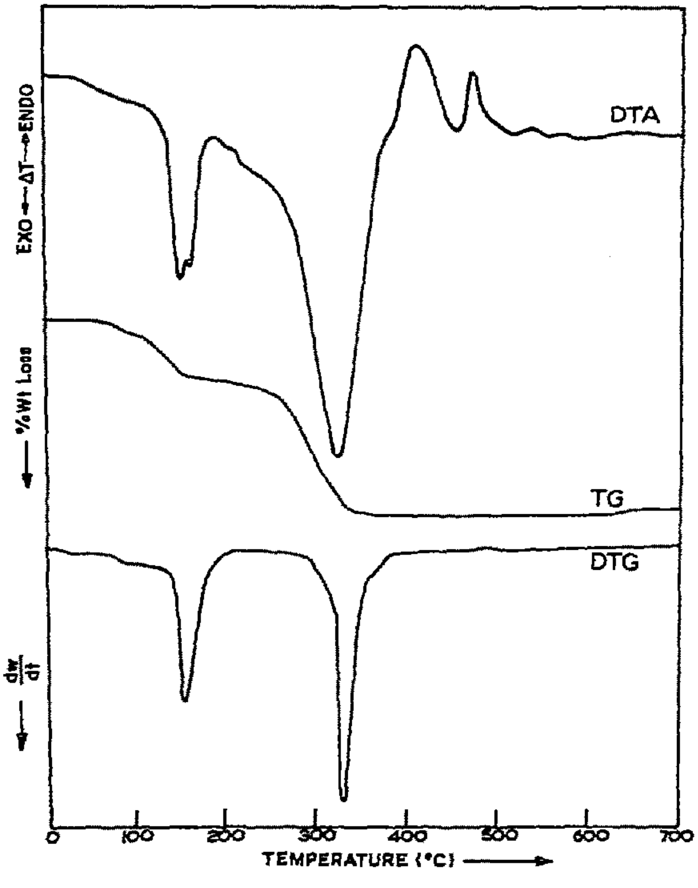

Fig. 2. DTA, TG and DTG of CdZrOx.

Decomposition of the oxalate

The decomposition of the oxalate is rather complex and the reaction takes place soon after the dehydration. At this stage the anhydrous CdZrOX decomposes to give directly a mixed oxide between 200—550°C. The weight loss in TG is 32.5%, compared with the calculated value of 30.0%. This indicates that the small amount of water which was held in the earlier step is also probably lost along with carbon monoxide and carbon dioxide. This change is very clear in DTA around 325°C and in DTG around 320°C. The experiment up to 800°C does not indicate any other change. In the DTA curve two exothermic peaks are observed, immediately following the decomposition of oxalate, at 415°C and 475°C (Fig. 2). The first peak at 415°C may be attributed to the oxidation of carbon monoxide and/or disproportionation of CO and the oxidation of the carbon produced. The other sharper exo-

TABLE 2

X-Ray powder diffraction data of cadmium zirconate

$\sin^2\theta$		Intensity I/I_1	*hkl*
Calcd.	Obsd.		
0.0155	0.0150	4	101
0.02475	0.0239	6	030
0.0440	0.0443	18	040
0.0493	0.0460 0.0476	14 4	122, 141
0.0620	0.0610	100	202
C.0731	0.0741	75	222
0.08675	0.0870	22	232
0.0874	0.0885	14	124
0.09315	0.0930	16	033
0.09585	0.0959	3	330
0.1227	0.1226	13	341
0.1247	0.1249	3	233
0.1262	0.1266	4	332
0.1474	0.1470	6	351
0.15115	0.1514	7	430
0.1735	0.1741	19	144
0.1815	0.1813	23	432
0.1835	0.1840	16	343
0.1900	0.1890	4	005
0.2082	0.2076	10	353
0.23065	0.2306	8	512
0.2390	0.2391	6	522
0.25075	0.2508	9	414
0.26625	0.2668	4	550
0.27275	0.2730	9	434

thermic peak around 475°C is probably due to the crystallization of the product formed during the oxalate decomposition. The IR spectrum of the end product cadmium zirconate is given in Fig. 1(b). The X-ray diffraction studies of the end product (isothermally obtained) using Cu*Kα* radiation indicate that the cadmium zirconate belongs to the orthorhombic crystal system with $a = 8.673_3$ Å, $b = 14.700_4$ Å and $c = 8.842_8$ Å. This is different to earlier data [13], which suggested a pseudocubic (monoclinic) crystal system with $a = 8.9$ Å and $\beta \sim 90°$. The indexing was done by Lipson and Steeple's method [14] and all the lines could be indexed into the orthorhombic system (a few lines of CdO were also observed). The values of $\sin^2\theta$ observed and calculated together with *hkl* and relative intensities are reported in Table 2.

The above results and discussions based on TG and other data indicate that cadmium zirconyl oxalate decomposes in a simpler way than other mixed metal oxalates [10—12] and is as follows

$$CdZrO(C_2O_4)_2 \cdot 5\ H_2O \xrightarrow{RT-190°C} CdZrO(C_2O_4)_2 + 5\ H_2O \tag{1}$$

$$CdZrO(C_2O_4)_2 \xrightarrow{190-550°C} CdZrO_3 + 2\ CO_2 + 2\ CO \tag{2}$$

After the decomposition of the oxalate a plateau is obtained in TG up to 800°C.

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