Acta Cryst. (1960). **13**, 749

The System Cadmium Oxide–Stannic Oxide

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(*Received* 14 *December* 1959)

In the course of a study of the system CdO–SnO_2 two compounds were formed by solid-state reactions. $CdSnO_3$ is orthorhombic with a distorted perovskite structure, having

$$a = 5{\cdot}547,\ b = 7{\cdot}867,\ c = 5{\cdot}577\ \text{Å}\ .$$

Cd_2SnO_4, not previously reported, is orthorhombic with

$$a = 10{\cdot}01,\ b = 5{\cdot}55,\ c = 3{\cdot}07\ \text{Å}\ .$$

The X-ray powder diffraction patterns of these compounds are given. Other phases of undetermined structure were obtained by heating cadmium α-stannate precipitates, but not by dry reaction.

Introduction

Compounds in the CdO–SnO_2 system may be prepared by two methods—by heating an intimate mixture containing appropriate proportions of suitable cadmium and tin compounds, or by precipitation from an alkali α-stannate solution of a cadmium compound, which is subsequently ignited. The former method was used by Náray-Szabó (1943), who reported the formation of a compound $CdSnO_3$ which, he stated, showed

Table 1. *Diffraction data for* $CdSnO_3$

Cu $K\alpha$ radiation (Film 32)

I	$\sin^2\theta_o$	$\sin^2\theta_c$	hkl
4b	0·0215	0·0200	100
3	0·0483	0·0487	111
4	0·0527		
10	0·0773	0·0777	121
5	0·0799	0·0798	200
3	0·0854	0·0861	012
2	0·1064	0·1061	112
		0·1061	031
		0·1069	130
1	0·1149	0·1151	022
2	0·1256	0·1260	131
5	0·1542	0·1546	040
7	0·1572	0·1563	202
1	0·1634	0·1634	032
2	0·1668	0·1668	230
5	0·1925	0·1920	103
		0·1936	141
4	0·2030	0·2016	113
1	0·2092	0·2084	311
1	0·2115	0·2106	023
8	0·2317	0·2306	123
		0·2310	042
4	0·2348	0·2344	240
8	0·2389	0·2374	321
2	0·2674	0·2666	330
2	0·2805	0·2806	151
2	0·2900	0·2905	223
2	0·2993		
2	0·3061	0·3058	004
7	0·3103	0·3108	242
1	0·3176	0·3179	052
2	0·3197	0·3194	400
		0·3213	250
1	0·3406	0·3405	251
1	0·3468	0·3465	143
1	0·3626	0·3613	313
6	0·3859	0·3856	204
5	0·3912	0·3903	323
5	0·3970	0·3978	252
1b	0·4061	0·4055	412
		0·4063	430
		0·4064	243
2	0·4257	0·4254	431
2	0·4337	0·4335	153
2	0·4394	0·4403	351
1	0·4481	0·4467	261
3	0·4613	0·4603	044
5	0·4745	0·4739	440
2b	0·5005	0·4990	500
		0·5010	413
4b	0·5100	0·5087	510
		0·5124	171
6b	0·5393	0·5397	163
		0·5402	244
4	0·5458	0·5464	054 α_1
2	0·5497	0·5491	054 α_2
4	0·5530	0·5523	270 α_1
2	0·5555	0·5550	270 α_2
		0·5559	521 α_1
5	0·5599	0·5600	450 α_1
3	0·5627	0·5627	450 α_2
2	0·5883		
2	0·6178	0·6172	080 α_1
1	0·6208	0·6202	080 α_2
3	0·6294	0·6286	272 α_1
2	0·6330	0·6317	272 α_2
2	0·6386	0·6389	344 α_1
1	0·6419	0·6421	344 α_2
2	0·6553	0·6562	181 α_1
		0·6563	305 α_1
3	0·6626	0·6627	424 α_1
3	0·6666	0·6660	424 α_2
		0·6660	460 α_1
		0·6660	315 α_1

Table 1 (*cont.*)

I	$\sin^2 \theta_o$	$\sin^2 \theta_c$	hkl
2	0·6710	0·6693	460 α_2
		0·6693	315 α_2
		0·6710	371 α_1
		0·6716	541 α_1
1	0·6751	0·6743	371 α_2
		0·6749	541 α_2
4	0·6946	0·6948	325 α_1
2	0·6963	0·6969	280 α_1
6	0·6996	0·6982	363 α_1
		0·6983	325 α_2
		0·7004	280 α_2
3	0·7027	0·7017	363 α_2
4	0·7134	0·7134	182 α_1
2	0·7170	0·7170	182 α_2
1	0·7229	0·7240	273 α_1
1	0·7262	0·7254	026 α_1
		0·7257	354 α_1
		0·7276	273 α_2
1	0·7306	0·7293	354 α_2
		0·7317	453 α_1
1	0·7353	0·7353	453 α_2
1	0·7419	0·7424	426 α_1
5	0·7730	0·7732	282 α_1
		0·7736	036 α_1
3	0·7771	0·7771	282 α_2
		0·7775	036 α_2
5	0·7813	0·7812	090 α_1
3	0·7850	0·7851	090 α_2
3	0·7979	0·7978	174 α_1
		0·7978	255 α_1
2	0·8017	0·8015	174 α_2
		0·8015	255 α_2
3	0·8091	0·8089	183 α_1
3	0·8134	0·8129	183 α_2
		0·8131	514 α_1
2	0·8180	0·8171	514 α_2
1	0·8248	0·8241	065 α_1
		0·8242	543 α_1
2	0·8295	0·8318	364 α_1
1	0·8342	0·8360	364 α_2
4	0·8456	0·8453	560 α_1
2	0·8500	0·8496	560 α_2
3	0·8575	0·8575	092 α_1
		0·8575	274 α_1
2	0·8610	0·8603	092 α_2
		0·8603	274 α_2
6	0·8661	0·8662	306 α_1
3	0·8700	0·8705	306 α_2
4	0·8751	0·8758	316 α_1
2	0·8791	0·8802	316 α_2
1	0·8825	0·8826	435 α_1
2	0·8995	0·8987	613 α_1
1	0·9034	0·9032	613 α_2
2	0·9125	0·9110	553 α_1
1	0·9147	0·9155	553 α_2
5	0·9347	0·9349	007 α_1
3	0·9391	0·9394	007 α_2
6	0·9498	0·9495	075 α_1
		0·9501	445 α_1
3	0·9542	0·9542	075 α_2
		0·9548	445 α_2
3	0·9581	0·9577	544 α_1
		0·9584	650 α_1
2	0·9628	0·9625	544 α_2
		0·9632	650 α_2
1	0·9686	0·9683	383 α_1
1	0·9712	0·9713	464 α_1
3	0·9778	0·9776	651 α_1
2	0·9829	0·9824	651 α_2
1	0·9866	0·9861	710 α_1

b indicates a broad reflection.

The reflections at $\sin^2 \theta = 0{\cdot}0527$ and 0·2993 are probably caused by uncombined stannic oxide, and so would indicate a very small loss of cadmium oxide from this originally stoichiometric preparation.

a monoclinic distorted perovskite structure and a lattice constant of 7·80 Å. According to Megaw (1946) such monoclinic structures are better described as orthorhombic. Coffeen (1953) reported a product with the formula $CdSnO_3$, prepared by the second method, and gave a table of unindexed interplanar spacings for it. These cannot be indexed on the basis of Náray-Szabó's unit cell. There does not appear to be in the literature any previous report of other compounds in this system.

Experimental and results

Solid-state reactions

Mixtures comprising various proportions of cadmium carbonate and stannic oxide were thoroughly ground and heated in air in alumina boats, by means of a platinum-wound resistance furnace. The powdered products were examined by X-ray diffraction using 9 cm. and 19 cm. diameter Unicam, Debye–Scherrer type cameras with filtered copper radiation. Wavelengths used were $K\alpha_1$ 1·54051, $K\alpha_2$ 1·54433 Å. Intensities of reflections were estimated visually on a scale of 10.

The products of firing at low temperatures were mixtures of cadmium and stannic oxides. After a long period (~ 40 hr.) at 800 °C. or a shorter period at 1000 °C. reaction occurred, and diffraction patterns showing the presence of mixed oxide phases were obtained. At these temperatures a small loss in weight, due to the volatilisation of cadmium oxide, was observed, and at higher temperatures this effect substantially altered the composition of the products. A specimen heated for one hour at 1240 °C. lost all its cadmium oxide, and the product consisted solely of the original stannic oxide, as was shown by the change in weight and by its X-ray diffraction pattern. Volatilisation of stannic oxide becomes appreciable at temperatures of about 1500 to 1600 °C. Most of the materials studied were prepared at various temperatures between 1000 and 1100 °C.

The powder diffraction patterns obtained showed the presence in the products of two mixed oxide phases in addition to the component single oxides. A pale yellow compound containing CdO and SnO_2 in the mole ratio 1:1, showed a distorted perovskite structure with orthorhombic symmetry. As the diffraction pattern closely resembled that of the cor-

Table 2. *Diffraction data for* Cd_2SnO_4

Cu $K\alpha$ radiation (Film 86)

I	$\sin^2\theta_o$	$\sin^2\theta_c$	hkl
1	0·0200	0·0193	010
1	0·0418	0·0429	210
8	0·0723	0·0724	310
2	0·0756	0·0772	020
		0·0777	$CdSnO_3$ line
10	0·0819	0·0802	CdO line
		0·0823	011
		0·0831	120
2	0·1147	0·1137	410
2	0·1303	0·1303	320
4	0·1396	0·1402	021
2	0·1538	0·1546	$CdSnO_3$ line
7	0·1575	0·1574	401
1	0·1733	0·1737	030
1	0·1774	0·1767	411
2	0·1952	0·1933	321
3	0·2171	0·2161	CdO line
1	0·2251	0·2247	520
8	0·2278	0·2268	330
4	0·2307	0·2298	511
3	0·2317	0·2317	610
2	0·2348	0·2346	421
2	0·2525	0·2520	002
2	0·2683	0·2681	430
1	0·2764	0·2754	601
		0·2756	202
1	0·2857	0·2877	521
3	0·2945	0·2947	611
		0·2949	212
6	0·3049	0·3051	302
2*b*	0·3281	0·3292	022
1*b*	0·3486	0·3464	402
2	0·3701	0·3714	711
2	0·3728	0·3718	041
2	0·3810	0·3823	322
2	0·3866	0·3861	630
3	0·4301	0·4293	721
		0·4316	132
2	0·4455		
3	0·4488	0·4491	631
		0·4493	232
3	0·4592	0·4599	811
1	0·5013		
1	0·5095		
1	0·5152	0·5159	CdO line
2	0·5217	0·5212	640
4	0·5262	0·5258	731
4	0·5466	0·5455	051
2	0·5606	0·5602	911
		0·5604	712
		0·5608	042
1	0·5751	0·5732	532
1	0·5915	0·5900	10,0,0
		0·5906	203
		0·5922	113
2	0·6048		
2	0·6244		
2	0·6338		
1	0·6386	0·6381	632
		0·6394	313
3	0·6609	0·6598	741 α_1
		0·6603	403 α_1
1	0·6646	0·6631	741 α_2
		0·6636	403 α_2
4	0·6941	0·6936	060 α_1
		0·6937	650 α_1
2	0·6968	0·6972	060 α_2
		0·6973	650 α_2
1	0·7008	0·6995	160 α_1
1	0·7045	0·7030	160 α_2
2	0·7123	0·7127	11,0,0 α_1
1	0·7163	0·7163	11,0,0 α_2
2	0·7194	0·7172	260 α_1
1	0·7237	0·7208	260 α_2
1	0·7347	0·7333	052 α_1
1	0·7381	0·7369	052 α_2
5	0·7422	0·7395	033 α_1
3	0·7463	0·7431	033 α_2
4	0·7520	0·7482	841 α_1
2	0·7562	0·7519	841 α_2
2	0·7931	0·7925	333 α_1
1	0·7970	0·7964	333 α_2
1	0·8075	0·8058	922 α_1
6	0·8107	0·8096	361 α_1
3	0·8147	0·8136	361 α_2
6	0·8359	0·8337	433 α_1
3	0·8398	0·8378	433 α_2
1	0·8434	0·8409	560 α_1
1	0·8474	0·8451	560 α_2
1	0·8616	0·8599	10,1,2 α_1
1	0·8655	0·8641	10,1,2 α_2
6	0·8964	0·8973	10,4,0 α_1
		0·8979	243 α_1
3	0·9010	0·9018	10,4,0 α_2
		0·9024	243 α_2
6	0·9114	0·9111	12,0,1 α_1
6	0·9159	0·9156	12,0,1 α_2
		0·9177	10,2,2 α_1
3	0·9204	0·9222	10,2,2 α_2
6	0·9273	0·9274	343 α_1
6	0·9310	0·9318	723 α_1
		0·9320	343 α_2
3	0·9351	0·9364	723 α_2
1	0·9435	0·9430	803 α_1
3	0·9451	0·9452	062 α_1
		0·9453	652 α_1
6	0·9500	0·9499	062 α_2
		0·9500	652 α_2
		0·9500	170 α_1
3	0·9544	0·9547	170 α_2
4	0·9640	0·9623	813 α_1
8	0·9650	0·9643	11,0,2 α_1
4	0·9700	0·9688	262 α_1
		0·9691	11,0,2 α_2
1	0·9755	0·9736	262 α_2
5	0·9818	0·9823	760 α_1
3	0·9864	0·9871	760 α_2
7	0·9883	0·9882	12,2,1 α_1
4	0·9932	0·9931	12,2,1 α_2

responding calcium compound, $CaSnO_3$, it was assumed that the extent of doubling of the pseudo-cell was the same as for that substance (Smith & Welch, 1960). The lattice constants for $CdSnO_3$, corrected for X-ray absorption in the specimen by extrapolation to $\theta=90°$ (Nelson & Riley, 1945), were found to be

$$a=5·547,\ b=7·867,\ c=5·577\ \text{Å}$$
$$\text{all}\ \pm 0·005\ \text{Å}\ .$$

These are mean values from several films, the data of one of which are reproduced in Table 1. The values obtained from different specimens, including those showing the presence of other phases, agreed within the experimental error, so that there appears to be no appreciable range of composition for this compound. Products approximating closely to the composition $CdSnO_3$ showed the presence of no other phases, provided that they had been sufficiently fired. It seems that the other mixed oxide, Cd_2SnO_4, is first formed, as insufficient firing (at temperatures less than 1100 °C.) of 1:1 CdO–SnO_2 mixtures led to a mixture of Cd_2SnO_4 with excess stannic oxide and a little of the perovskite phase. Refiring of such mixtures caused further reaction and led to the production of pure, or nearly pure, $CdSnO_3$.

The diffraction pattern of the bright yellow product corresponding with the formula Cd_2SnO_4 always showed weak lines due to the presence of cadmium oxide or the perovskite phase or both, but these were at a minimum when the mole ratio of CdO to SnO_2 in the product was 2:1. The colour of the products reached a maximum intensity at about this composition. The diffraction pattern of Cd_2SnO_4 was indexed on the basis of an orthorhombic unit cell with

$$a=10{\cdot}01,\ b=5{\cdot}55,\ c=3{\cdot}07\ \text{Å}\ ,$$

these figures having been obtained from the single crystal measurements referred to below. As the structure is not pseudo-cubic, these values were not corrected for X-ray absorption. The data from a typical film are shown in Table 2.

Products prepared by solid-state reactions ranged in composition from 10 to 90 moles of cadmium oxide per cent. One unexplained diffraction line of medium intensity appeared in a few patterns from tin-rich products prepared at temperatures of 1050 °C. or less, but no other evidence for other mixed oxide phases than the two described above was obtained.

Solution reactions

A number of samples were prepared by treating a solution of potassium α-stannate with cadmium ions, and subsequently heating the white precipitates obtained, to remove the water content. At low temperatures of ignition (600 to 800 °C.) the yellow anhydrous materials gave complex diffraction patterns, which showed differences according to the proportions of cadmium and stannate ions used for the precipitation, and have not yet been satisfactorily interpreted. Neither of the mixed oxides described above seemed to be present, but some of the lines observed also occur in Coffeen's (1953) data. One of these materials on heating at 1000 °C. gave a product showing the perovskite structure of $CdSnO_3$.

Single crystals

Various molten salts were used as solvents in attempts to grow crystals of cadmium tin oxides suitable for X-ray studies. The only success was achieved when a melt of cadmium chloride, to which cadmium and stannic oxides had been added, was evaporated for seven hours at 800 °C. in a current of air. Microscopic examination of the part of the product which was insoluble in water revealed several phases, one of which occurred in yellow, oblong, weakly birefringent crystals large enough for X-ray work. One of these was selected, and rotation and oscillation patterns taken showed it to be orthorhombic with

$$a=10{\cdot}01\pm0{\cdot}02,\ b=5{\cdot}55\pm0{\cdot}01,\ c=3{\cdot}07\pm0{\cdot}01\ \text{Å}\ .$$

It was considered that the yellow crystals were of Cd_2SnO_4 as their diffraction pattern and colour are both concordant with this conclusion.

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