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An X-ray diffraction study of the system Al_2Se_3–In_2Se_3 in the In-rich region.*

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Abstract

A series of samples in the system Al_2Se_3–In_2Se_3 in the In-rich region have been synthesized and studied by X-ray diffraction. In the interval of the Al/In (molar) ratio r from $r \gtrsim 1/50$ to $r \lesssim 1/20$ the system has a two-phase region, $\alpha + \gamma_1$, where α is isostructural with the room-temperature modification of In_2Se_3, and γ_1 is isostructural with the second high-temperature modification, γ, of In_2Se_3. For $r \gtrsim 1/20$, ternary γ_1 alloys $(Al_xIn_{1-x})_2Se_3$ are present alone and their unit-cell parameters decrease continuously as the Al content increases. These results are analogous with those obtained for the system Ga_2Se_3–In_2Se_3 in the In-rich region. The samples have also been studied by differential thermal analysis and electron-probe microanalysis.

Introduction

The first synthesis of a semiconductor ternary alloy $(Al_xIn_{1-x})_2Se_3$, with $x = 1/7$, was reported recently by Desnica, Desnica & Etlinger (1978), together with a study of some physical properties (electrical conductivity, photosensitivity). We here report a systematic study of the system Al_2Se_3–In_2Se_3, with the Al/In (molar) ratio r changing from 0 to ~ 1. To our best knowledge, these potentially important semiconducting alloys, having energy gaps in the visible portion of the optical spectrum, have not been synthesized and studied previously. This may be mainly because the constituents have quite different vapour pressures, so that the very high vapour pressure of Se is a great problem at the temperatures used in conventional methods of crystal growth. This problem has been circumvented using a modified SSD (solid, solute, diffusion) technique of crystal growth (Etlinger, 1976). The SSD method, used originally for growth of GaP crystals (Kaneko, Ayabe, Dosen, Morizane, Usui & Watanabe, 1973), has turned out to be very convenient for growing various compounds whose constituents have essentially different vapour pressures, as for instance the alloys $(Al_xIn_{1-x})_2S_3$ (Etlinger, 1976; Popović, Etlinger & Gržeta-Plenković, 1978).

The structural parameters of the synthesized samples have been studied and the results are described in the present paper. A systematic investigation of semiconducting properties is in progress and will be published elsewhere.

Experimental

The essential characteristics of the SSD technique used in preparation of the samples in the system Al_2Se_3–In_2Se_3 were as follows (Desnica, Desnica & Etlinger, 1978). The mixture of Al + In (purity 6*N*), for a given molar ratio *r*, was placed in an alumina crucible in the upper part of an evacuated reaction vessel. At the top of the mixture the temperature was ~ 1220 K during the synthesis (several days). Se (purity 5*N*8) was placed in the lower part of the vessel, where temperature was ~ 990 K (this corresponded to $\sim 1{\cdot}5 \times 10^5$ Pa of selenium vapour pressure). The temperature gradient along the reaction vessel was approximately 5 K mm^{-1}. Se evaporated and diffused into the melted Al + In. When the reaction was complete, the prepared sample was slowly cooled to room temperature over 10 h. The samples were compact polycrystalline ingots with colour changing from black to dark-red, reddish and orange with increasing Al content. Attempts to prepare stable samples in the Al-rich region, for $r \gtrsim 1$ up to $r \simeq 2$, were not successful.

The structural properties of the samples were examined by X-ray diffraction, using a counter diffractometer with monochromatized Cu $K\alpha$ radiation [$\lambda(\alpha_1) = 1{\cdot}54051$, $\lambda(\alpha_2) = 1{\cdot}54433$ Å]. The unit-cell parameters and *d* values of the alloys were determined with ZnO as internal standard [$a = 3{\cdot}249\,(1)$, $c = 5{\cdot}205\,(1)$ Å]. The samples were also studied by differential thermal analysis (DTA) and electron-probe microanalysis.

Results and discussion

The crystal data for the synthesized samples are given in Table

Table 1. *Crystal data for the samples in the system* Al_2Se_3–In_2Se_3 *in the* In-*rich region at room temperature* (298 K)

r is the Al/In molar ratio and *x* is the concentration of Al. The data for γ-In_2Se_3 are also given for comparison with phase γ_1.

r = Al/In	x	phase	space group	unit-cell parameters (Å)		U (Å^3)	Z	D_x(Mg m^{-3})
0		$\alpha(R)$	$R\bar{3}m$	$a_{\alpha(R)} = 4{\cdot}025(5)$;	$c_{\alpha(R)} = 28{\cdot}762(7)$	403·5	3	5·757
1/49		$\alpha(R)+\gamma_1$		$a_{\alpha(H)} = 4{\cdot}025(5)$;	$c_{\alpha(H)} = 19{\cdot}235(5)$	269·9	2	5·739
		or						
		$\alpha(H)+\gamma_1$		$a_{\gamma_1} = 7{\cdot}119(3)$;	$c_{\gamma_1} = 19{\cdot}26(2)$	845·3	6	5·415
1/24		$\gamma_1+\alpha$		$a_{\gamma_1} = 7{\cdot}119(3)$;	$c_{\gamma_1} = 19{\cdot}26(2)$	845·3	6	5·415
1/12	1/13	γ_1	$P6_1$ or $P6_5$	$a_{\gamma_1} = 7{\cdot}098(4)$;	$c_{\gamma_1} = 19{\cdot}25(2)$	839·9	6	5·373
1/6	1/7	γ_1	$P6_1$ or $P6_5$	$a_{\gamma_1} = 7{\cdot}086(2)$;	$c_{\gamma_1} = 19{\cdot}206(15)$	835·2	6	5·266
1/2	1/3	γ_1	$P6_1$ or $P6_5$	$a_{\gamma_1} = 7{\cdot}020(2)$;	$c_{\gamma_1} = 18{\cdot}993(16)$	810·6	6	5·014
9/11	9/20	γ_1	$P6_1$ or $P6_5$	$a_{\gamma_1} = 6{\cdot}975(4)$;	$c_{\gamma_1} = 18{\cdot}850(12)$	794·2	6	4·860
0		γ(803 K)	$P6_1$ or $P6_5$	$a_{\gamma} = 7{\cdot}133(10)$;	$c_{\gamma} = 19{\cdot}58(2)$	862·7	6	5·396
0		γ(298 K)	$P6_1$ or $P6_5$	$a_{\gamma} = 7{\cdot}130(10)$;	$c_{\gamma} = 19{\cdot}430(15)$	855·4	6	5·442

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1. For $r=0$, the black alloy obtained was α, rhombohedral, In_2Se_3. The same phase was also obtained by the usual direct synthesis of In and Se in exact stoichiometric amounts in evacuated silica tubes (Popović, Čelustka & Bidjin, 1971; Popović, Tonejc, Gržeta-Plenković, Čelustka & Trojko, 1979).

At low contents of Al, *e.g.* for $r=1/49$ and $r=1/24$, the samples were mixtures of α and γ_1 phases, where γ_1 is isostructural with the second high-temperature modification, γ, of In_2Se_3. The crystal data of γ-In_2Se_3 are also given in Table 1, at 803 and 298 K (as it can be undercooled and be stable at room temperature; Tonejc, Popović & Gržeta-Plenković, 1980). In the sample with $r=1/49$, the fractions of α and γ_1 phases were similar. But in the sample with $r=1/24$ the phase γ_1 was dominant with, say, 1% of α phase. The α phase in these two samples was either rhombohedral (R) or hexagonal (H) (Popović, Čelustka & Bidjin, 1971; Popović, Tonejc, Gržeta-Plenković, Čelustka & Trojko, 1979). The unit-cell parameters of α and γ_1 phases in this two-phase region practically did not change with the Al content, the parameters of the α phase being equal to the values for α-In_2Se_3. DTA of the sample with $r=1/49$ showed five distinct signals. Four of them were interpreted to correspond to the α phase (Popović, Tonejc, Gržeta-Plenković, Čelustka & Trojko, 1979): 473 K (transition $\alpha\rightarrow\beta$), 793 K ($\beta\rightarrow\gamma$), 1003 K ($\gamma\rightarrow\delta$) and 1153 K (melting point). The fifth signal at 1115 K corresponded to the melting point of the γ_1 phase.

For greater contents of Al, *i.e.* for r greater than $\simeq 1/20$, up to $r\simeq 1$, the samples were ternary alloys $(Al_xIn_{1-x})_2Se_3$, designated as γ_1. The unit-cell parameters of these ternary alloys decreased continuously as the Al content increased.

The dependence of unit-cell parameters on the Al/In molar ratio, r, and on the concentration of Al, x, is shown in Fig. 1 in terms of normalized parameters, a_N and c_N, defined as follows:

$$(a_N)_\alpha = a_\alpha;\ (a_N)_{\gamma_1,\gamma} = a_{\gamma_1,\gamma}/3^{1/2}\ ;$$
$$(c_N)_\alpha = c_{\alpha(R)}/3,\ \text{or}\ c_{\alpha(H)}/2;\ (c_N)_{\gamma_1,\gamma} = c_{\gamma_1,\gamma}/2\,.$$

As a_N and c_N for different phases are analogous parameters in the same crystal directions, they can be directly compared. One can see that the normalized unit-cell parameters change abruptly at the $\alpha\rightarrow\gamma_1$ transition: a_N by 2·11%, c_N by 0·47%

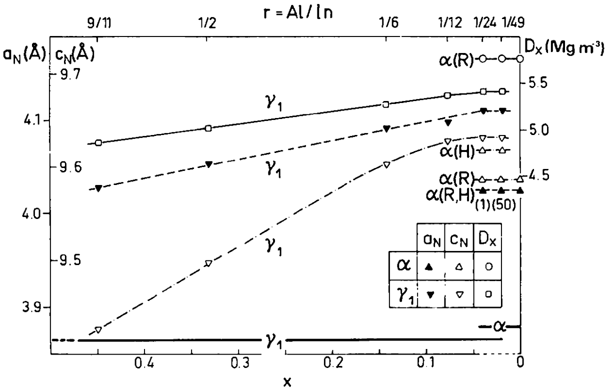

Fig. 1. Dependence of normalized unit-cell parameters, a_N and c_N, and density, D_x, on the Al/In molar ratio, r, and on the concentration of Al, x, for the samples in the system Al_2Se_3–In_2Se_3. Figures in parentheses represent the approximate percentage of the α (R, H) phase in the two-phase region.

Table 2. *Powder diffraction data for* $(Al_{1/7}In_{6/7})_2Se_3$(298 K)

d_{obs} (Å)	d_{calc} (Å)	*hkl*	I/I_0
5·84	5·85	101	10
5·17	5·17	102	27
3·78	3·78	104	2
3·545	3·543	110	100
3·322	3·324	112	2
3·255	3·256	105	9
3·205	3·201	006	≫100
3·100	3·100	113	8
3·028	3·030	201	17
2·923	2·923	202	25
2·852	2·851	114	1
2·766	2·767	203	1
2·586	2·586	204	1
2·503	2·505	107	4
2·398	2·397	205	9
2·374	2·375	116	48
2·302	2·303	211	13
2·254	2·255	212	18
2·237	2·236	108	32
2·180	2·181	213	1
2·087	2·089	214	3
2·045	2·046	300	50
1·985	1·986	215	8
1·890	1·891	208	18
1·880	1·878	216	2
1·832	1·833	1,0,10	5
1·827	1·828	119	11
1·805	1·806	305	2
1·771	1·772 1·771	220 217	8
1·750	1·752	209	2
1·723	1·724	306	35
1·707	1·707	223	2
1·675	1·676	312	3
1·667	1·668	218	16
1·638	1·640	307	1
1·601	1·601	0,0,12	7
1·550	1·550	226	4
1·481	1·479	2,1,10	1
1·458	1·459	1,1,12	3
1·436	1·436	1,0,13	3
1·403	1·404	321	4
1·393	1·395 1·393	2,1,11 322	5
1·389	1·388	318	4
1·374	1·375	323	1
1·365	1·363	229	2
1·350	1·351	324	1
1·338	1·339 1·339 1·339 1·336	410 407 1,0,14 411	12
1·331	1·331 1·331	2,0,13 319	3
1·322	1·322	325	3
1·311	1·311	413	2
1·261	1·261	3,0,12	4
1·252	1·253 1·253 1·252	1,0,15 327 2,0,14	6
1·245	1·246 1·246 1·244	2,1,13 409 2,2,11	1
1·235	1·235	416	4
1·224	1·225	501	2
1·217	1·217 1·219	502 3,1,11	3
1·214	1·214	328	6

Table 2 (*cont.*)

d_{obs} (Å)	d_{calc} (Å)	*hkl*	I/I_0
1·204	1·205	503	2
	1·204	1,1,15	
	1·203	417	
1·188	1·189	504	2
	1·188	2,2,12	
1·181	1·182	2,0,15	9
	1·181	330	
	1·181	2,1,14	
	1·179	331	
1·175	1·175	329	1
1·135	1·137	1,1,16	2
	1·135	3,2,10	
	1·135	2,2,13	
	1·134	419	
1·116	1·118	2,0,16	1
	1·116	3,1,13	
1·110	1·111	1,0,17	2
	1·110	425	
1·108	1·108	336	4
	1·108	4,0,12	
1·100	1·100	511	3
	1·098	4,1,10	
1·092	1·093	508	3
	1·090	426	
1·068	1·068	427	3
	1·068	3,1,14	
	1·067	0,0,18	
	1·066	2,1,16	
1·064	1·064	509	2
	1·064	4,0,13	
	1·063	4,1,11	
1·058	1·060	2,0,17	2
	1·060	338	
	1·059	515	
	1·057	3,2,12	
1·043	1·044	428	2
	1·042	516	
1·022	1·023	3,1,15	3
	1·023	517	
	1·023	600	
	1·023	4,0,14	
	1·021	601	
1·001	1·003	432	2
	1·002	518	
0·9824	0·9825	3,2,14	2
0·9738	0·9739	5,0,12	2
0·9490	0·9488	1,0,20	1
0·9468	0·9469	437	1
0·9249	0·9251	527	1
0·9166	0·9165	2,0,20	1
0·9145	0·9147	5,0,14	2

Table 3. *Powder diffraction data for* $(Al_{1/3}In_{2/3})_2Se_3$(298 K)

d_{obs} (Å)	d_{calc} (Å)	*hkl*	I/I_0
5·79	5·79	101	14
5·12	5·12	102	31
3·73	3·74	104	1
3·512	3·510	110	100
3·295	3·292	112	1
3·220	3·221	105	6
3·166	3·166	006	$\geqslant$ 100
3·068	3·070	113	11
3·000	3·002	201	20
2·894	2·895	202	30
2·560	2·560	204	3
2·475	2·478	107	6

Table 3 (*cont.*)

d_{obs} (Å)	d_{calc} (Å)	*hkl*	I/I_0
2·372	2·373	205	8
2·352	2·351	116	47
2·281	2·281	211	11
2·233	2·233	212	17
2·212	2·211	108	32
2·068	2·068	214	3
2·027	2·027	300	72
1·966	1·966	215	6
1·871	1·871	208	18
1·858	1·860	216	2
1·808	1·809	119	8
1·754	1·755	220	10
	1·754	217	
1·733	1·734	209	1
1·706	1·707	306	34
1·679	1·680	311	1
1·659	1·660	312	2
1·650	1·651	218	14
1·623	1·624	307	1
1·589	1·589	314	2
1·583	1·583	0,0,12	9
1·535	1·535	226	7
1·488	1·488	316	1
1·464	1·464	2,1,10	1
1·448	1·448	404	1
1·442	1·443	1,1,12	3
1·421	1·421	1,0,13	2
1·391	1·391	321	3
1·380	1·380	2,1,11	4
	1·380	322	
1·375	1·375	318	2
1·348	1·349	229	1
1·338	1·338	324	1
1·325	1·327	410	11
	1·326	407	
	1·324	1,0,14	
	1·323	411	
1·317	1·317	2,0,13	3
	1·317	319	
1·309	1·309	325	2
1·298	1·298	413	1
1·247	1·247	3,0,12	4
1·239	1·240	1,0,15	6
	1·240	327	
	1·239	2,0,14	
1·233	1·233	2,1,13	2
	1·233	409	
1·224	1·224	416	3
1·213	1·213	501	1
1·206	1·206	502	2
	1·206	3,1,11	
1·203	1·203	328	4
1·191	1·192	4,1,7	1
	1·191	1,1,15	
1·169	1·170	330	6
	1·169	2,0,15	
	1·168	2,1,14	
	1·168	331	
1·159	1·158	418	1
	1·158	505	
1·141	1·141	4,0,11	1
	1·141	422	
1·124	1·125	1,1,16	2
	1·124	3,2,10	
	1·123	2,2,13	
	1·123	419	
1·097	1·099	1,0,17	3
	1·097	336	
	1·096	4,0,12	

Table 3 (*cont.*)

d_{obs} (Å)	d_{calc} (Å)	*hkl*	I/I_0
1·084	1·085 1·085	3,2,11 512	2
1·081	1·082 1·080	508 426	1
1·056	1·058 1·057 1·055 1·055	427 3,1,14 0,0,18 2,1,16	3
1·054	1·054 1·053 1·052	509 4,0,13 4,1,11	1
1·049	1·049 1·049 1·049	2,0,17 338 515	1
1·013	1·013 1·013 1·013 1·012 1·012	3,1,15 517 600 4,0,14 601	3
0·9920	0·9920	518	1
0·9865	0·9864	1,0,19	1
0·9726	0·9728 0·9725	4,0,15 3,2,14	3
0·9642	0·9642	5,0,12	1
0·9407	0·9409	3,3,12	1
0·9380	0·9383 0·9379	1,0,20 437	3
0·9162	0·9160 0·9163	4,1,15 527	1
0·9063	0·9064	2,0,20	2

[$\alpha(R)\rightarrow\gamma_1$] or by 0·15% [$\alpha(H)\rightarrow\gamma_1$]. Powder diffractometer data for the alloys with $x=1/7$ and $x=1/3$ are given in Tables 2 and 3.

DTA of the ternary, γ_1, alloys for $x \gtrsim 1/20$ gives only one signal at 1115 (5) K corresponding to the melting point. The dependence of the melting point of the synthesized samples on r and x is shown in Fig. 2, together with the DTA curve for the alloy with $x=1/3$.

All these results are quite similar to those obtained for the system Ga_2Se_3–In_2Se_3 in the In-rich region (Popović, Čelustka, Ružić-Toroš & Broz, 1977; Tonejc, Popović & Gržeta-Plenković, 1980).

The investigation of the alloys in the γ_1 phase by electron-probe microanalysis has confirmed the composition given by

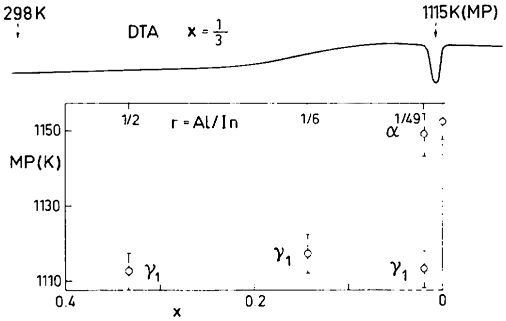

Fig. 2. Dependence of the melting point, MP, on the Al/In molar ratio, r, and on the concentration of Al, x, for the samples in the system Al_2Se_3–In_2Se_3. The DTA curve for the alloy $(Al_{1/3}In_{2/3})_2Se_3$ is also shown.

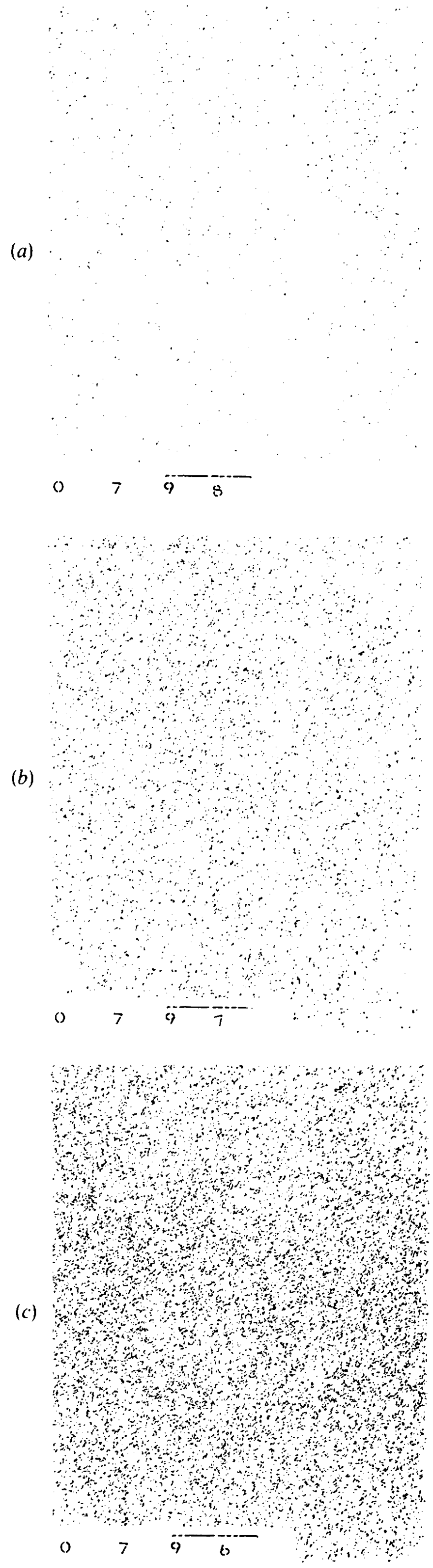

Fig. 3. Distribution of (*a*) *Al*, (*b*) In and (*c*) Se in the alloy $(Al_{1/3}In_{2/3})_2Se_3$ as found by electron-probe microanalysis.

the chemical formula, within the limits of experimental error. Moreover, it has been confirmed that the distribution of all the elements, Al, In and Se, is uniform, as is shown in Fig. 3(*a*), (*b*), (*c*) for the alloy with $x = 1/3$.

References

Desnica, D., Desnica, U. & Etlinger, B. (1978). *Fizika* (*Zagreb*), **10**, *Suppl.* 2, 29–33.

Etlinger, B. (1976). *Proc. 13th Int. Conf. Physics of Semiconductors, Rome* 1976, edited by F. G. Fumi, pp. 501–504. Amsterdam: North Holland.

Kaneko, K., Ayabe, M., Dosen, M., Morizane, K., Usui, S. & Watanabe, N. (1973). *Proc. IEEE*, **61**, 884–890.

Popović, S., Čelustka, B. & Bidjin, D. (1971). *Phys. Status Solidi A*, **6**, 301–304.

Popović, S., Čelustka, B., Ružić-Toroš, Ž. & Broz, D. (1977). *Phys. Status Solidi A*, **41**, 255–262.

Popović, S., Etlinger, B. & Gržeta-Plenković, B. (1978). *Fizika* (*Zagreb*), **10**, *Suppl.* 2, 84–88.

Popović, S., Tonejc, A., Gržeta-Plenković, B., Čelustka, B. & Trojko, R. (1979). *J. Appl. Cryst.* **12**, 416–420.

Tonejc, A., Popović, S. & Gržeta-Plenković, B. (1980). *J. Appl. Cryst.* **13**, 24–30.

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Crystal data for a third polymorph (γ) of C.I. Pigment Red 1,1-[(4-nitrophenyl)azo]-2-naphthol.

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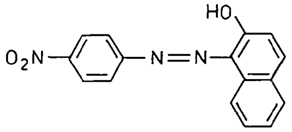
Abstract

The preliminary single-crystal data and powder pattern are given for a third polymorph of C.I. Pigment Red 1. The powder pattern has been indexed using the single-crystal dimensions; the problems of multiple indexing have been reduced by comparison with single-crystal intensities and calculated structure factors.

Origin of specimen

C.I. Pigment Red 1 (C.I. 12070), $C_{16}H_{11}N_3O_3$, is given the molecular structure



and during the early stages of the crystal-structure determination it was noticed that no powder diffraction data existed. Single crystals were obtained by making a saturated solution of the commercial pigment, Monolite Fast Red BS, in chlorobenzene at 353 K. This was placed in an oven and the temperature raised to 358 K to ensure complete solution of the pigment. The solution was slowly cooled to room temperature over a period of about two weeks.

Optical examination

The crystals were deep-red and blade shaped up to 1 × 0·4 × 0·05 mm in size and showed a monoclinic aspect with a monoclinic angle of about 107°.

The crystals exhibited oblique extinction on the blade face, but the extinctions were not sharp. One extinction direction was approximately parallel to the length of the crystal, being about 5° from it in the obtuse angle.

X-ray examination

Laue photographs showed that the crystals belong to the

Table 1. *X-ray powder data for the γ form of C.I. Pigment Red* 1

d_{obs}	*hkl*	d_{calc}	*I*
12·91	020	12·999	17
7·38	100	7·355	12
7·09	110	7·077	32
6·40	120	6·401	43
5·94	021	5·912	12
5·74	$11\bar{1}$	5·746	17
5·60	130	5·607	49
5·37	$12\bar{1}$	5·367	6
4·87	140	4·870	40
4·62	041	4·644	22
4·33	060	4·333	15
4·27	111	4·263	15
3·89	$15\bar{1}$	3·899	5
3·65	200 210 141	3·677 3·641 3·599	17
3·488	$16\bar{1}$	3·491	18
3·414	$11\bar{2}$	3·410	53
3·308	$12\bar{2}$ 151 002 012	3·326 3·323 3·319 3·293	100
3·210	022	3·216	62
3·056	$25\bar{1}$	3·031	10
2·870	$22\bar{2}$ $15\bar{2}$ $18\bar{1}$	2·873 2·869 2·846	7
2·809	260	2·804	8
2·757	$23\bar{2}$	2·789	5
2·703	190	2·689	5
2·631	$27\bar{1}$ 241 270	2·632 2·626 2·613	9
2·596	0,10,0 181	2·600 2·597	7
2·558	$31\bar{1}$	2·553	7
2·525	142 $32\bar{1}$	2·518 2·517	7
2·469	$33\bar{1}$	2·460	4
2·401	320	2·409	2*
2·367	$18\bar{2}$ 330	2·362 2·359	5

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