

The cadmium oxide - tungsten oxide phase system and growth of cadmium tungstate single crystals

D. S. ROBERTSON, I. M. YOUNG

Royal Signals and Radar Establishment, Malvern, Worcestershire, UK

J. R. TELFER

Rank-Hilger Ltd, Margate, UK

The results of a further study of the cadmium oxide-tungsten oxide phase diagram are presented and the results of attempts to prepare single crystals of cadmium tungstate. The defects encountered in the crystals and attempts to eliminate them are described and the best conditions for growth of high-quality single crystals detailed. The relationship of the defects to the crystal growth mechanism is discussed.

1. Introduction

Single crystals of cadmium tungstate were first produced with centimetre dimensions by Gillette [1]. The crystals were pale yellow-green and were produced by the Verneuil method. Spitkovskii and Pashkovskii [2] produced crystals by the Czochralski technique and described some of the defects encountered. This work reports the results of further study of the cadmium oxide-tungsten oxide phase diagram and the growth of single crystals. The relationship of the growth defects encountered to the crystal growth mechanisms is discussed.

2. Experiments

The phase diagram was studied by means of differential thermal analysis, Debye-Scherrer X-ray powder diffraction photography and attempts to grow crystals. The region of the diagram studied was from 41 mol% through 50 mol% to 60 mol%. The mixtures were prepared from commercially available compounds whose total metallic impurity content was stated as less than 10 ppm. Crystal growth was performed using equipment previously described [3]. Melting was performed in 50 mm diameter 50 mm deep platinum crucibles using radio-frequency heating and various flowing gas ambients were tested. The melts were produced from mixtures of the component oxides, which were best sintered at 1000°C for 12 h before melting, as the shrinkage is considerable, from

the reaction between ammonium tungstate and cadmium oxide, when fired together and from cadmium tungstate precipitated from solutions of sodium tungstate and cadmium nitrate, when mixed. After growth, recharging of the crucible with cadmium oxide plus previous melts, with cadmium oxide plus one of the previous starting materials and with cadmium oxide plus crystalline material, were investigated. Regrowth from melts formed entirely of crystalline material was also investigated. Growth rates in the range 1 to 4 mm h⁻¹ were attempted using no rotation and rotation rates of 10 and 40 rpm. Changing the direction of rotation [4] every 30 sec at a rotation rate of 25 rpm was also investigated. Crystals were grown with [100], [001], 10° from [001] and 45° from [001] as growth axes.

3. Results

The differential thermal analysis results were as follows. Experiments showed that mixed oxide samples would fully sinter in air after 10 h at 900°C or 2 h at 1000°C. Sintering at any higher temperature caused increasing loss of cadmium oxide from the mixture. These samples were then subjected to heating to 1300°C and cooling at a rate of 10°C min⁻¹ in the DTA apparatus. The heating cycle was then repeated, and the endothermic peak on the recycle, corresponding to melting, was always observed to have moved. The temperature of the observed peaks are plotted against composition in

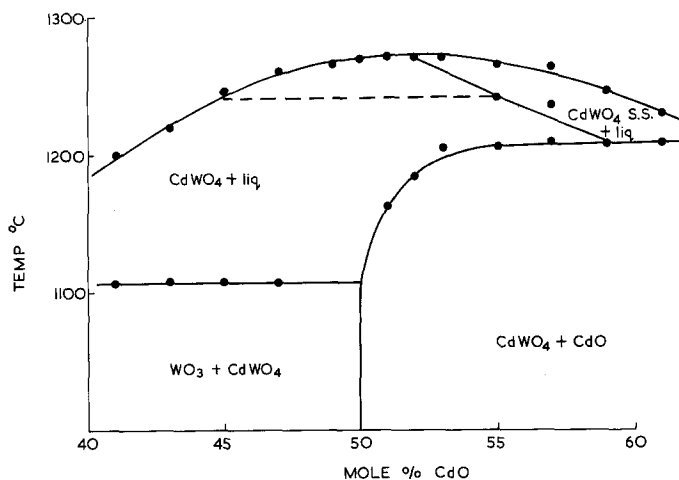


Figure 1 The system CdO/WO₃ 40 to 60 mol % CdO. Solidus temperature 40 to 50 mol % CdO 1106 ± 3° C; phase change in CdWO₄, 1240° C; maximum liquidus melting point 1272 ± 3° C; solidus temperature 55 mol% CdO and above 1260 ± 3° C.

Fig. 1 and a proposed liquidus and solidi are shown. A dotted line has been included at 1240° C, which represents a peak that occurred no higher than this on each cooling cycle of material with a liquidus temperature above 1240° C. This extra peak, however, was not observed on the heating cycles. Samples of single crystal when subjected to the above DTA procedure showed only a single peak on the first heating cycle but three peaks on subsequent cooling cycles.

X-ray diffraction studies of sintered powders gave the following results. Powder photographs of samples 45 to 55 mol% cadmium oxide showed essentially lines corresponding to the monoclinic cadmium tungstate (wolframite) structure, but in the photographs of samples sintered as outlined above, the presence of tungsten trioxide was detected from the presence of extra lines in all samples with a mol% cadmium oxide less than or equal to 49. In the case of the sample 51 mol% cadmium oxide, it was not possible to identify diffraction lines indicative of excess cadmium oxide but in samples 53 and 55 mol% cadmium oxide the presence of free cadmium oxide was detected. In sintered samples 50, 51, 53 and 55 mol% cadmium oxide there are two weak low-angle lines on the powder photographs which are not attributable to the cadmium oxide, tungsten oxide or cadmium tungstate (wolframite) structures. Other extra lines not belonging to cadmium oxide or tungsten oxide are observed in a sample of 50 mol% quenched to room temperature.

Powder photographs of single crystal material of differing colour were indistinguishable from each other, and showed none of the extra lines described above. Visual inspection of precipitated

material liberally washed with water and dried at 90° C in a vacuum oven showed it to be micro-crystalline. This was supported by the powder photograph of the dried precipitate, which, although not producing very sharp diffraction lines, undoubtedly showed the pattern of the monoclinic wolframite phase of cadmium tungstate. Firing of this precipitate in air at 300, 500, 900, and 1250° C did not produce any other pattern of lines, but merely improved the crystallinity of the material.

The results of attempts to produce single crystals were as follows. Crystal growth is made difficult by the considerable vaporization from the melt. This amounts to 12.0 g h⁻¹ maximum. The component vaporizing is principally cadmium oxide although some tungsten oxide is also lost. Accurate analysis proved difficult since deposition was uneven in various parts of the equipment. The result of this is that the melting point of the molten material in the crucible is continually changing. The fact that crystals could be produced arises from the flat form of the liquidus curve of the phase diagram around the 50 mol% point. However, this changing melting point would inevitably lead to decrease in the diameter of the growing crystal in a constant thermal field. Thus as growth proceeded, the temperature was slowly and automatically lowered to compensate for the effect. Figs. 2 to 4 show samples of crystals produced. These are cleaved sections since there is a cleavage plane perpendicular to [0 1 0] and crystals grown with [0 0 1] as axial direction show a pronounced facet normal to this direction. Crystals grown with [1 0 0] as axial direction also exhibit a pair of planar faces corresponding to (0 0 1) planes. Fig. 5 shows a

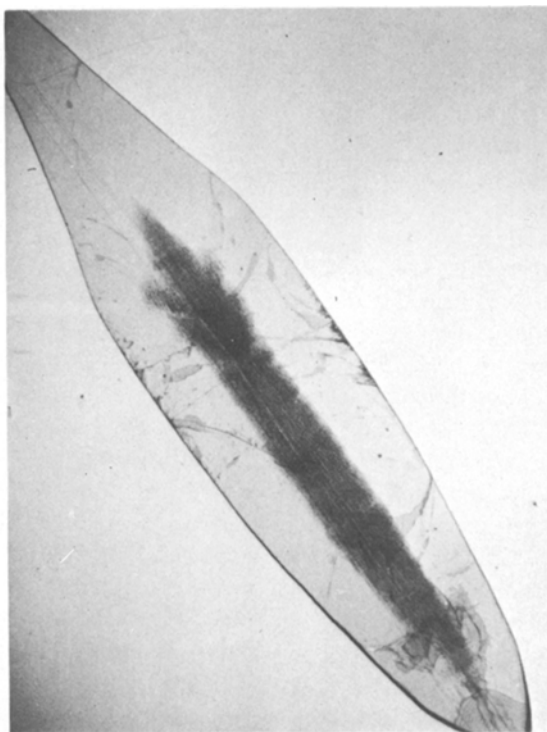


Figure 2 Cadmium tungstate single crystal [001] showing typical core ($\times 1.3$).

section of a [100] crystal parallel to the interface. All crystals exhibited cores.

The colour of the crystals can be colourless,

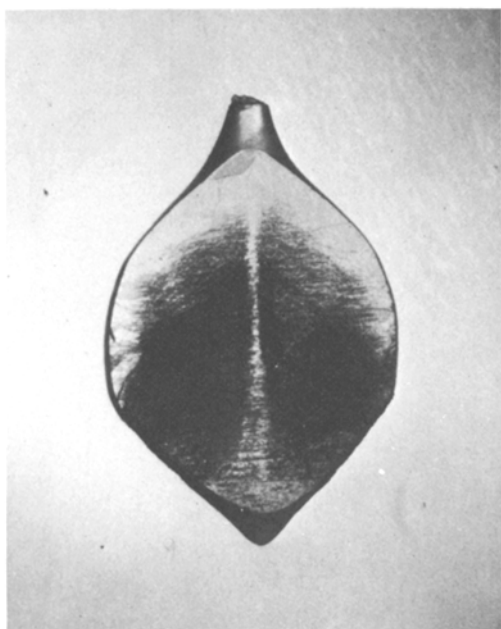


Figure 3 Cadmium tungstate single crystal [100] showing split core ($\times 1.3$).

yellow, orange, pale green, translucent deep green and black. These colour effects could arise from impurities, stoichiometry changes and gas ambient used, and were investigated by means of visible and ultraviolet spectra and electron-beam excitation and study of growth conditions and melts.

Visible and ultraviolet transmission spectra were produced from three samples each about 4 mm thick and being colourless, pale yellow, yellow-orange. The spectra are shown in Fig. 6: though nominally similar for 800 to 500 nm, they differ below 500 nm. The colourless sample shows approximately the same transmission from 800 to 350 nm where the ultraviolet cut-off commences smoothly, reaching 1% transmission at 325 nm. The pale yellow sample shows the presence of two absorption bands, one about 400 nm and the other about 350 nm, the orange shows these two bands with larger amplitude and the ultraviolet cut-off at longer wavelength. In the latter the 400 nm band is very broad, and the tail extends past 500 nm. The onset of colour of the material is probably related to the appearance of this absorption band. Annealing experiments were conducted on single crystal samples to ascertain whether a colour change could be effected. Samples heated

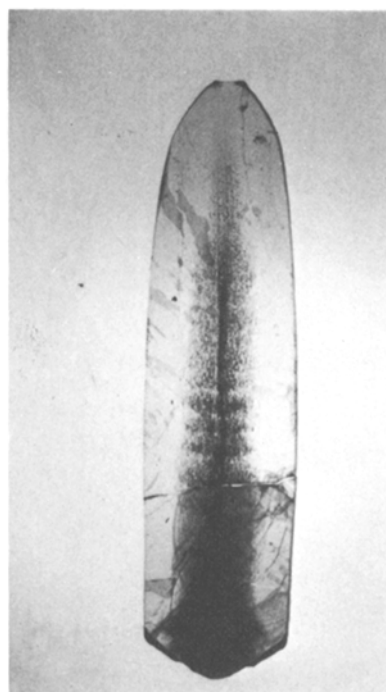


Figure 4 Cadmium tungstate single crystal [001] showing effect of rotation reversal ($\times 1.3$).

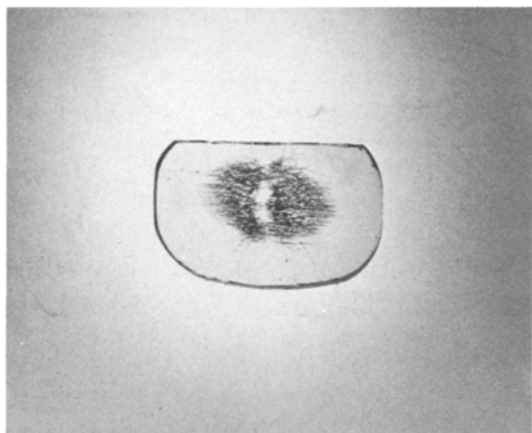


Figure 5 A section of [100] crystal parallel to the interface.

in air or oxygen to 1150° C showed severe thermal etching demonstrated on a cleaved surface. Samples annealed at 1100° C showed no apparent change in optical transmission, except when annealed in argon or nitrogen when the surface of the sample acquired a grey covering considered to be tungsten caused by the ready reduction of the tungstate to free metal. This latter effect was observed during crystal growth in pure nitrogen or argon which gave rise to black crystals.

Phosphor measurements using 20kV, μsec , pulsed electron excitation on samples of cadmium tungstate prepared by sintering in air at 1000° C for 12 h and then grinding to less than 50 μm particles size, showed a variation in luminescence with stoichiometry at 490 nm in the region around

50 mol%. The maximum light output of about 20% of Ag/ZnS standard phosphor was observed from the stoichiometric composition, the intensity falling off with a slight excess of either phase. Precipitated material shows a very dim blue luminescence which might be expected as the powder photograph shows the precipitate though poorly crystalline to be in the wolframite phase. Firing for 12 h at various temperatures up to 1000° C increases the luminescence progressively. Firing at 1250° C shows a decrease in luminescence over that heated to 1000° C.

Two different samples of powdered single crystal, less than 50 μm particle size, under electron excitation showed differing outputs, both below the output of sintered 49, 50, 51 mol% mixed oxides. The first crystal, lighter in colour, had the lesser output of the pair. Finally, phosphor measurements of sintered powders deliberately doped with impurity ions such as copper, silver and manganese all produced much lower outputs than undoped material. These results showed that impurities and gas ambient affect crystal colour, and crystals were hence grown from very pure starting materials in an atmosphere of air flowing at 500 ml min⁻¹.

To determine the effect of stoichiometry on colour, growth was performed from a 500 g melt formed from previously used melts in flowing air atmosphere. The colour of the crystal obtained was translucent green.

Without changing any growth conditions, a second crystal was grown from the remaining melt

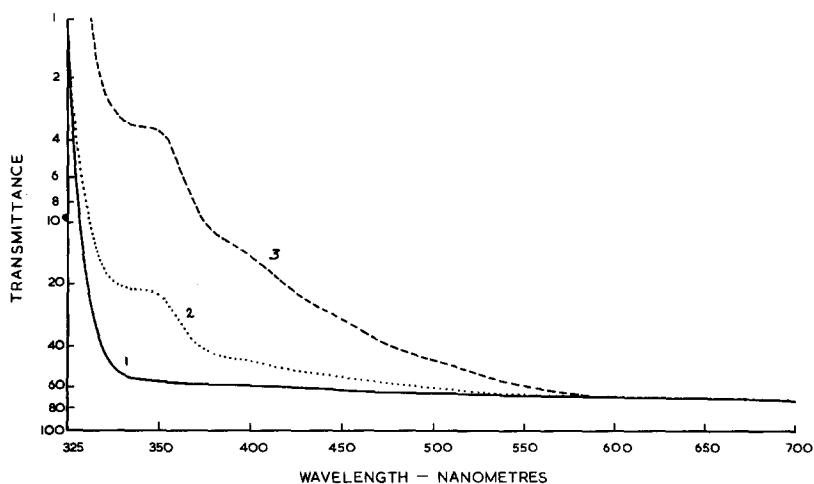


Figure 6 Visible/ultraviolet transmission spectra of 4 mm thick samples of CdWO₄ (1) colourless, (2) pale yellow, (3) yellow orange.

from above, to which had been added a weight of used melt equal to that of the crystal produced, a weight of pure cadmium oxide equal to the measured weight loss, plus cadmium oxide in addition. This procedure was repeated until the weight of cadmium oxide added, in excess of the weight loss, reached 100 g. Since tungsten oxide is lost from the melt as well as cadmium oxide, this procedure gradually changed the melt from tungsten oxide-rich to cadmium oxide-rich. The results of these tests were that the core persisted until at least 50 g of cadmium oxide over the weight loss was added. This amounted to 25% of the weight of grown crystal. The crystals produced in this series gradually became orange in colour and the core diminished.

The translucent deep green colour of some crystals as described is the result of the major defect in these crystals. This is the formation of cores. These cores occur irrespective of the orientation of the growth axis used and confirm the results of previous workers [2]. There are, however, differences in the nature of the cores. In the [1 0 0] grown crystals the core is split (Fig. 3). This effect has been observed in [0 1 0] crystals previously [2] and is very reminiscent of the split domain effect in single crystal lithium niobate [5]. The core in crystals grown with the [0 0 1] as axial direction do not show the cores splitting (Fig. 2). In every case the core commences some time after initiation of growth and always starts at the centre of the crystal. These facts strongly indicated the presence of a facet on the interface. The presence of a facet was sought in core-free samples of [1 0 0] crystals by means of Twyman–Green tests. These tests failed to confirm definitely the presence of facets in [0 0 1] and [1 0 0] crystals. A core also appeared in [0 0 1] crystals grown without rotation, and it took the same form as that in [0 0 1] crystals grown with rotation.

Changes in the growth rate, rotation rate and the direction of rotation during growth failed to eliminate the cores, although the latter did tend to concentrate the core in a manner similar to impurity concentration in zinc tungstate grown under oscillatory motion [4]. The core region was shown by X-ray fluorescence to be tungsten-rich and this was confirmed by the fact that crystals growth from slightly cadmium oxide-rich melts were free of core for a greater length than those grown from stoichiometric melts. Attempts to eliminate the core by change of axis of growth to

10° and 45° from [0 0 1] also did not eliminate the core although it tended to be displaced to one side (Fig. 7). The core often widened to the full crystal diameter (Fig. 4) giving a translucent deep green appearance to the crystal. If growth was attempted from tungsten oxide-rich melts, the core effect encompassed the whole crystal almost from the beginning of growth giving the entire crystal this latter appearance. Growth from cadmium oxide-rich melts produced crystals with much reduced coring. Study of melts showed that those prepared from cadmium-rich mixtures and cooled immediately after melting, were formed of crystalline material in the form of long laths, whose colour was either colourless or pale yellow depending on the purity of starting material. Those remaining after growth were invariably translucent green and were composed of compact microcrystals. Growth of crystals from melts prepared from remelted single crystals did not produce improved crystals.

The loss in weight was highest when growth was performed from cadmium oxide-rich melts reaching as high as 12.0 g h^{-1} and lowest when growth was performed using remaining melts from previous

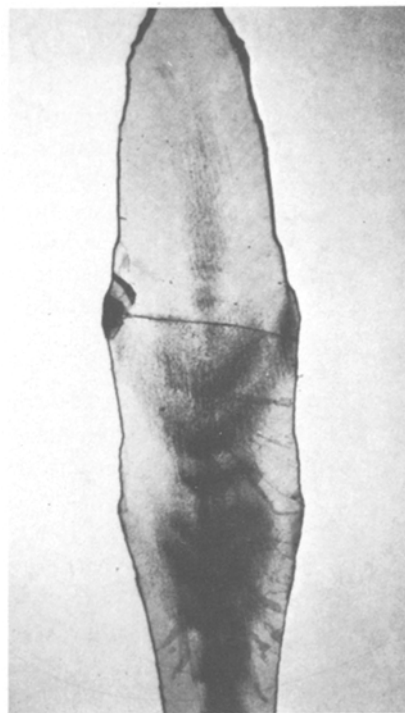


Figure 7 Cadmium tungstate single crystal [0 0 1] showing core displacement due to off-axis growth by 10° ($\times 1.3$).

growths which were tungsten oxide-rich. The loss in the latter case being 0.2 g h^{-1} . The weight loss from cadmium oxide-rich melts slowly diminished during growth.

On completion of growth, the remaining melt could amount to 50% of the initial charge of relatively expensive components: attempts were made to re-use the remainder. However, a rapid accurate analysis was necessary to decide the ratio of the components to be added to allow re-use. Samples of sintered oxides and powdered crystal were subjected to electron-beam excitation and the output plotted as a function of stoichiometry. In the range 47 to 53 mol% cadmium oxide a variation was observed in the light output. The intensity fell rapidly with excess of either phase over stoichiometric composition as previously stated, in a manner similar to that observed in the magnesium oxide-tungsten oxide system [6]. However, when melts were subjected to this test the results were not precise enough to define the composition. Thus to re-use melts, an empirical procedure adopted. It was assumed that the measured weight loss was entirely cadmium oxide and that the crystals with little coring were also cadmium-rich. Hence, the additions made to a used melt were a weight of starting material equal to 75% of the grown crystal and a weight of cadmium oxide equal to the remainder plus the weight loss. The starting material could be used melt (tungsten oxide-rich), mixed oxides (cadmium oxide-rich), precipitated material (stoichiometric), and single crystal pieces (cadmium oxide-rich). In all cases the correct nature of the melt could be confirmed by its crystalline appearance. However, melts could only be re-used three or four times as the crystals became more coloured due to impurity accumulation.

To summarize these results, the best conditions for growth of high quality cadmium tungstate are growth from a melt 5 mol% rich in cadmium oxide, formed in platinum crucibles, from starting materials with less than 10 ppm total metallic ion content at a growth rate of 3 to 5 mm h^{-1} , a rotation rate of 40 rpm, with [001] as the axial direction, in an atmosphere of flowing air at 500 ml min^{-1} . Continuous automatic temperature reduction at a rate of $0.5^\circ \text{ C h}^{-1}$ is also advisable. Under these conditions the crystals will be colourless at best and very pale yellow at worst. However, all will have a core present to some

extent but this is minimized by growth under the above conditions.

4. Discussion

During the preparation of cadmium tungstate crystals as described, the following observations were made: various peaks in the DTA studies, extra lines in the X-ray patterns, variations in colour and luminescent intensity under electron-beam excitation and the presence of tungsten oxide-rich cores in the crystals.

The DTA results, plotted in Fig. 1 show a maximum point of $1272 \pm 3^\circ \text{ C}$, though apparently not at 50% mole composition. The eutectic temperature of $1108 \pm 3^\circ \text{ C}$ between tungsten oxide and cadmium tungstate and the other eutectic temperature, $1206 \pm 3^\circ \text{ C}$, both agree well with the published values [8]. Other peaks observed in 55 and 57 mol% cadmium oxide samples suggest a region of solid solution. The third peak observed on the cooling cycles of 45 to 55 mol% samples is indicated by a dotted line, as its position varied with the amount of supercooling of the molten sample, but once occurred as high as 1240° C . The presence of this peak suggests the existence of a high-temperature phase similar to that observed in magnesium tungstate [20]. The reason that this peak only occurs on the cooling cycles of the DTA runs may be explained either on the assumption of a phase change, irreversible in the solid state, or on the basis of the endothermic peak, corresponding to melting, being sufficiently broad to obscure the phase change peak. This phase change was not suggested in previous work [8] but here the authors only used 45, 50 and 55 mol% samples, so may well have failed to observe the extra DTA peak.

Melting samples of 50 mol%, quenched to room temperature, produced a number of extra lines in the powder photograph in addition to those of the wolframite phase. The extra lines, none of which correspond to tungsten oxide or cadmium oxide, appear to show a similar pattern to those observed for the high-temperature phase of magnesium tungstate [7]. The d spacings observed in the case of cadmium tungstate are about 1.03 times those recorded for magnesium tungstate, a similar factor to the a/a and b/b ratio for cadmium tungstate and magnesium tungstate, and the ratio of atomic radii $r_{\text{Ca}}/r_{\text{Mg}}$.

Thus it would appear there may be a high-temperature phase of cadmium tungstate, though

whether the phase change is fully reversible in the solid state is not known.

The origin of the two low-angle diffraction lines observed, with d spacings 9.90 and 8.34 Å in 50 to 55 mol% cadmium oxide sintered samples and also in precipitated material calcined at 1000°C, is less easy to identify. None of the materials so far identified have a large enough cell to produce such low-angle diffraction lines. By comparison with magnesium tungstate, where a cubic phase exists with a 12.8 Å cell edge, it might be envisaged that the cadmium tungstate observed line $d = 9.90$ Å was equivalent to the very strong 110 reflection of magnesium tungstate. The only other strong line of the cubic magnesium tungstate diffraction photograph would occur about 2.8 Å, which corresponds to a similar theta value to one of the lines from monoclinic cadmium tungstate. Hence, though it is inconclusive, there is some evidence to suggest that cadmium tungstate may also, during sintering, produce a cubic phase, which is apparently stabilized to some extent by excess cadmium oxide.

With respect to the colour variations, there is evidence of crystal and melt colours, absorption spectra and photoluminescence measurements. Crystals and melts formed from cadmium oxide-rich conditions were colourless or pale yellow, whereas those formed from tungsten oxide-rich conditions were green, and those formed by re-using melts were always orange. It is evident, therefore, that purity decides the colour in the former conditions. The absorption spectra lends some support to this conclusion. The sharper band at about 350 nm is probably due to a structural defect and the colour band to a metallic ion impurity. This impurity is likely to be a transition metal ion since the presence of iron was detected in most starting materials except the precipitated materials, which had the lowest metallic impurity, the main one being sodium presumably retained from soluble sodium tungstate used in preparation. It was from this material, made to 55 mol% with very pure cadmium oxide, which nearly always produced colourless crystals. The part played by the defect in colouring the crystals is less certain, since there is still controversy [9–11] about the activity of the tungsten sites.

The photoluminescence results add some weight to the postulation that colour is affected by impurities since the output is reduced by metallic ion additions as reported both here and in the

literature [8, 9]. Some transition elements quench luminescence, those elements which more strongly colour the crystals having the greatest effect. However, in this case the fact that stoichiometry variations decreased the output, that powdered single crystal outputs are below that of 49, 50 and 51 mol% sintered samples, and that sintering in nitrogen decreased the output in contrast to calcium tungstate [12], means that these results are ambiguous.

Finally, there is the formation of cores. These are tungsten oxide-rich regions in the crystal and the excess of tungsten oxide in the melt arises from the continuous loss of cadmium oxide. Thus, in this system, one of the crystal components eventually acts in a manner akin to high concentration of impurity not readily accepted by the crystal, i.e. an impurity with a low segregation coefficient (k). The effect of such an impurity has been studied and treated theoretically by a number of investigators [12–17]. In the work of Tiller *et al.* [16] the result of the above circumstances is that the growing interface disintegrates when the supercooling induced ahead of the interface by the difference in mass and thermal flows exceeds a specific value. This treatment invokes a transient period of growth, while the impurity at the interface rises to a set value and thereafter the conditions at the interface are considered to be near equilibrium. The formation of cores in these crystals supports this hypothesis in that the initial parts of the crystal are core-free. The extent of this region is much greater than would be expected from theoretical treatment, but it must be remembered that until the loss of cadmium oxide has been sufficient to materially affect melt composition, no “impurity” is present. The onset of interface disintegration at the centre of the crystal interface in the case of [001] crystals and at points away from the centre of the interface separated by a clear region in the case of [010] crystals, presents difficulties. An explanation of the effect would be that the temperature gradients at points from the centre to the edge were different and that at some point conditions for interface disintegration were met by the changes in thermal flow rather than mass flow. However, the evidence shows the core to have a sharp boundary implying a sudden change in thermal flow at this point. This seems to be very unlikely especially in the cases of [010] crystals. The work of Hurle [18] who modified the theoretical treatment of Tiller *et al.*

to include the fact that there is considerable fluid flow in a Czochralski growth system, should thus be applicable. However, this treatment assumed the interface to be planar, and hence that the fluid flow could be treated in the manner of Cochran [19]. Thus the onset of interface disintegration would be uniform over the interface, which in this instance is plainly not the case.

The only real explanation of the effects observed must nevertheless involve fluid flow, but the nature of the flow over the interface cannot be as postulated [18]. It is known that the thermal fluid flow in melts of compounds like cadmium tungstate is very strong, much stronger than in melts of high thermal conductivity materials (metals) or high viscosity materials (glasses). In addition, it has been demonstrated that hydrodynamic fluid flow induced by continuous crystal rotation does not readily overcome thermal fluid flow [20] and that thermal fluid flow can only be overcome by crystals rotation reversal [4]. This latter fact is supported by the effect of rotation reversal which concentrated the core. The fact that the core appeared in crystals grown without rotation is additional evidence of the presence of thermal fluid flow. Thus it is concluded that the thermal fluid flow is the dominant impurity distribution mechanism. This fluid flow, which arises at the walls of the crucible flows across the liquid surface and down the centre of the melt, is in the reverse direction to hydrodynamic fluid flow and causes conditions at the interface which deviate from the theoretical treatments. The analysis of this situation is difficult mathematically. However, the evidence of this work indicates that impurity accumulation at the centre of the interface is the result, and the conditions for interface breakdown are first attained at this point. The situation in the case of [100] crystals is difficult to explain, more especially since the presence of facets was not confirmed. The only reasonable explanation is that the interface is dominated by growth on two major facets inclined at an angle to each other (Fig. 3) and that where they intersect at the centre of the interface impurity accumulation has been reduced by removal on the growing facets.

In conclusion, the above work has shown that high-quality cadmium tungstate crystals can be grown, and it is confirmed that this is the only compound in the cadmium oxide–tungsten oxide phase diagram that can be formed as single crystals.

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References

1. R. M. GILLETTE, *Rev. Sci. Instrum.* **21** (1950) 294.
2. I. M. SPITKOVSKII and M. V. PASHKOVSKII, *Sov. Phys. Cryst.* **16** (1972) 729.
3. B. COCKAYNE, D. S. ROBERTSON and W. BARDSLEY, *Brit. J. Appl. Phys.* **15** (1964) 1165.
4. H. A. CHEDZEY and D. S. ROBERTSON, *J. Phys. D.* **5** (1972) 325.
5. H. T. PARFITT and D. S. ROBERTSON, *Brit. J. Appl. Phys.* **18** (1967) 1079.
6. C. G. HILL, *Trans. Farad. Soc.* **42** (1946) 685.
7. J. FONDA, *J. Phys. Chem.* **48** (1944) 303.
8. I. KISLYAKOV and B. LOPATIN, *Russ. J. Inorg. Chem.* **12** (1967) 1673.
9. J. W. MARDEN and G. MEISTER, *Trans. Illum. Eng. Soc.* **34** (1939) 503.
10. F. A. KROGER, "Some aspects of luminescence in solids" (Elsevier, Amsterdam, 1948) p. 136.
11. G. BORN, A. HOESTAETTER, A. SCHARMANN and G. SCHWARZ, *J. Lumin.* **1** (1970) 641.
12. A. M. GURVICH, *ibid* **15** (1977) 187.
13. G. H. GULLIVER, "Metallic Alloys" (Griffin, London, 1922) Appendix.
14. E. SCHEUER, *Z. Metallk.* **23** (1931) 237.
15. A. HAYES and J. CHIPMAN, *Trans. AIME* **135** (1939) 85.
16. W. A. TILLER, K. JACKSON, J. RUTTER and B. CHALMERS, *Acta. Met.* **1** (1953) 428.
17. W. BARDSLEY, J. S. BOULTON and D. T. J. HURLE, *Sol. State Elect.* **5** (1962) 395.
18. D. T. J. HURLE, *Solid State Electronics* **3** (1961) 37.
19. W. G. COCHRAN, *Proc. Camb. Phil. Soc.* **30** (1934) 365.
20. D. S. ROBERTSON, *Brit. J. Appl. Phys.* **17** (1966) 1047.

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