of u increases with increasing amount of Mg. This indicates that the incorporation of Mg ions in the ZnO lattice causes an attraction between the cations and the basal plane. The decrease in u for Ca-doped ZnO up to 3 mol% is considered to result primarily from an expansion of the lattice due to the incorporation of Ca ions; the increase in u with further increase in Ca amount is attributed to some effects of the segregated CaO on the grain boundaries of ZnO. B_{eff} (the value for pure ZnO is taken as 1.0) for Mg-doped ZnO decreased at first, and then increased up to 10 mol% Mg. For Ca-doped ZnO, B_{eff} showed changes similar to those for Mg-doped ZnO. The initial decrease in B_{eff} is considered to result from the strain generated in the lattice by the incorporation of foreign ions producing local stress which leads to a suppression of atomic vibration. The increase in B_{eff} observed with addition of foreign ions may be caused by segregation of MgO or CaO on the grain boundaries, which has an influence on the surface states of the ZnO particles. We also observed that excess MgO, CaO and SrO form amorphous layers on the surface of the ZnO lattice; the details will be reported in a future publication.

References

1. E. R. SEGNIT and A. E. HOLLAND, *J. Amer. Ceram. Soc.* **48** (1965) 409.
2. G. D. ARCHARD, *Acta Cryst.* **6** (1953) 657.
3. M. INAGAKI, H. FURUHASHI and S. NAKA, *Bunko-kenkyu* **21** (1972) 202.
4. H. FURUHASHI, M. INAGAKI and S. NAKA, *J. Inorg. Nucl. Chem.* (1973) 3009.
5. V. V. NITTS, E. G. PAPULOVA, I. SOSNOVSKAYA, and E. SOSNOVSKIJ, *Fiz. Tver. Tela.* **6** (1964) 1369.
6. S. C. ABRAHAMS and J. L. BERNSTEIN, *Acta Cryst.* **25** (1969) 1233.
7. T. M. SABINE and S. HOGG, *Acta Cryst.* **25** (1969) 2254.

Received 6 October 1980
and accepted 9 April 1981

F. HAYASHI
T. UEMATSU
H. HASHIMOTO
Faculty of Engineering,
Chiba University,
Yayoicho, Chiba-shi,
Japan

Phase relationships and their effect on cathodoluminscence in the yttrium oxide–tungsten oxide system

Rare-earth tungstates as host lattices for rare-earth luminescent ions have been widely studied. The original work was performed by Borchardt [1, 2] and subsequently work was done by Van Uitert [3] Nassau [4] and Blasse [5]. Not all of this work specifically involved the tungstates of yttrium with trivalent europium as the emitting ion. For example Van Uitert [3] studied trivalent europium only in tungstate lattices which had the scheelite structure and Blasse [5] studied mixed tungstate–molydate lattices. With reference to the present work the experiments of Borchardt [1, 2] are most relevant.

Borchardt gave an outline phase diagram of the yttrium oxide–tungsten oxide system which indicated that four compounds exist. Of these, only one melted congruently, another melted incongruently and the remainder did not melt. Borchardt also gave the minimum temperature of formation and limited crystallographic data. He also studied the emission of two undoped tungstates, when irradiated by light of wavelength 253.7 nm at both room temperature and liquid nitrogen temperature. He found that both emitted light at about 450 nm. One emitted strongly at low temperature only and the other emitted strongly at both low and room temperatures. The work recorded below is a further study of the luminescent properties of the compounds in the yttrium–tungstate phase diagram with special reference to how the luminescence is affected by stoichiometry as given by the diagram.

The starting materials used were commercially available high purity yttrium oxide and tungsten oxide. The former was subjected to cathode-ray tube tests for impurities and the spectra showed no significant amounts of any other rare-earth ions.

The phosphors were all prepared in the following manner. The appropriate quantities of the

0022–2461/81/113229–5$02.50/0

powders were weighed and mixed by milling together in a plastic capsule containing agate cylinders for 30 min using pure water as the lubricating fluid. The mixture was transferred to a platinum crucible and heated to the appropriate temperature in a chosen atmosphere for the appropriate time. The firing time does not include heating-up and cooling-down times. Following this, samples were obtained by passing the powder through a sieve which had a pore size of 38 μm. The completeness of reaction was followed by X-ray powder photographs taken after various firing times.

The preparation of luminescent targets was performed as follows. The mounts used were 6 mm diameter, 2 mm thick aluminium discs. The powder layers were mounted on these discs by centrifugal settling from slurries made in dry propanol. The discs were held in a depression cut into the top of a rubber stopper which fitted loosely in a 50 cm^3 round-bottom centrifuge tube. The disc and stopper were placed in the base of the tube and the slurry inserted. After centrifugation the stopper was extracted by means of wire handles attached to it and the disc was removed.

The phosphor was activated by an electron beam operating at various powers and the data were recorded on an $X-Y$ recorder. Intensity comparisons were made using targets of standard phosphors operating in the appropriate region of the visible spectrum.

The compounds existing in the phase diagram are Y_2O_3, $3WO_3$, $Y_2O_3WO_3$, $15Y_2O_39WO_3$, $9Y_2O_34WO_3$ and $3Y_2O_3WO_3$. The compound $Y_2O_33WO_3$ melts congruently and $Y_2O_3WO_3$ melts incongruently. Borchardt [1, 2] has shown that both emit under photoluminescence at 450 nm, the former only emitting at low temperatures, the latter at all temperatures up to room temperature.

Preliminary preparations of all compounds were made using trivalent europium as the emitting ion. The firing time and the firing temperature were 8 h and 1200° C and the atmosphere was air. These were tested for luminescence and it was established that only normal ytterium tungstate $Y_2(WO_4)_3$ and yttrium oxytungstate (Y_2WO_6) emit at 615 nm with Eu^{3+} ion as the emitting ion. These compounds were also observed to emit at 450 nm as found by Borchardt [1, 2] using photoluminescence. The emission intensity at 615 and 415 nm was measured at the various concentrations of trivalent europium ion used, by comparison against a commercial preparation of yttrium vanadate with trivalent europium as the emitting ion.

The two compounds were then submitted to preparation at various temperatures and the results are shown in Table I. From Table I it can be seen that $Y_2(WO_4)_3$ is the better phosphor and that as the weight per cent of europium oxide increases the emission intensity reaches a maximum in each case. The only atmosphere of preparation to induce any effect is hydrogen. There is a considerable variation in the results at a given weight per cent of dopant in non-reducing atmospheres. Table II records the effect of increasing dopant concentration on the lattice emission of Y_2WO_6 prepared under various conditions. These show that the intensity of lattice emission gradually decreases as the dopant concentration increases. Fig. 1 records the effects of changing stoichiometric ratios of the compounds Y_2O_3 and WO_3 at a fixed dopant concentration and fixed preparation conditions. Each point is the mean of several preparations. In addition the liquidus of the yttrium oxide–tungsten oxide phase system is shown for comparison [1].

The results above establish that in the yttrium oxide–tungsten oxide phosphor system stoichiometry plays an important role in the efficiency of emission. The form of the emission intensity curve closely follows that of the liquidus curve on the phase diagram given by Borchardt [1]. The conclusion from this is that even small amounts of a second phase in a phosphor function as an energy-loss mechanism. The results also show that although both tungstates show blue lattice emission, the oxytungstate has the most intense emission and is the poorer host for Eu^{3+} emitting ions. Further, the lattice emission is suppressed by increases in the concentration of Eu^{3+} ions. Borchardt [2] explained this on the basis of the lattice emission originating at tungstate ions and energy being transferred to the emitting rare-earth ion. However, this does not seem to be entirely the case on the above evidence. It seems most likely that lattice emission is another energy-loss mechanism. The suppression of lattice emission by high concentrations of Eu^{3+} implies that the former emitting centres are progressively occupied by the latter ions, suppressing the emission, Thus it can

TABLE I Emission intensity at 615 nm for various doped yttrium–oxygen–tungsten compounds under different preparation conditions

Compound formula	Eu_2O_3 dopant (wt %)	Emission intensity at 615 nm						
		Air, 8 h, 1200° C	Air, 8 h, 1400° C	100 % O_2, 8 h, 1200° C*	100 % N_2, 8 h, 1200° C	100 % H_2, 8 h, 500° C	100 % H_2, 8 h, 1000° C	Reoxidized 100 % O_2, 8 h, 1200° C
Y_2WO_6	0.1	1.9	6.6	4.0, 5.7	7.6	1.8	1.6	6.4
Y_2WO_6	1.0	12.2	20.0	12.0, 14.2	15.3	16.3	2.2	13.2
Y_2WO_6	5.0	13.1	20.0	19.0, 11.4	15.3	14.5	3.5	20.0
Y_2WO_6	10.0	5.2	9.4	16.3, 9.3	7.6	6.2	zero	11.1
$Y_2(WO_4)_3$	0.1	13.7	15.2	14.8, 12.4	15.3	12.2	zero	13.6
$Y_2(WO_4)_3$	1.0	59.1	47.3	42.5, 46.2	46.1	34.4	zero	54.0
$Y_2(WO_4)_3$	5.0	45.8	56.5	78.7, 59.3	92.4	59.1	zero	88.6
$Y_2(WO_4)_3$	10.0	14.2	52.1	55.3, 28.1	54.8	46.8	zero	55.5
Y_2O_3	0.1	–	–	–	–	–	–	–
Y_2O_3	1.0	16.8	–	–	–	–	–	–
Y_2O_3	5.0	–	–	29.1	–	–	–	–
WO_3	1.0	zero	–	–	–	–	–	–

*Results from two series

TABLE II Emission intensity at 450 nm for doped Y_2WO_6 under different preparation conditions

Compound formula	Eu_2O_3 dopant (wt %)	Emission intensity at 450 nm						
		Air, 8 h, 1200° C	Air, 8 h, 1400° C	100 % O_2, 8 h, 1200° C	100 % N_2, 8 h, 1200° C	100 % H_2, 8 h, 500° C	100 % H_2, 8 h, 1000° C	Reoxidized 100 % O_2, 8 h, 1200° C
Y_2WO_6	zero	25	20	29	10	12	13	16
Y_2WO_6	0.1	39	18	19	10	12	9	14
Y_2WO_6	1.0	24	10	17	10	7	6	11
Y_2WO_6	5.0	9	3	6	zero	2	1	4
Y_2WO_6	10.0	2	6	11	zero.	2	zero	zero

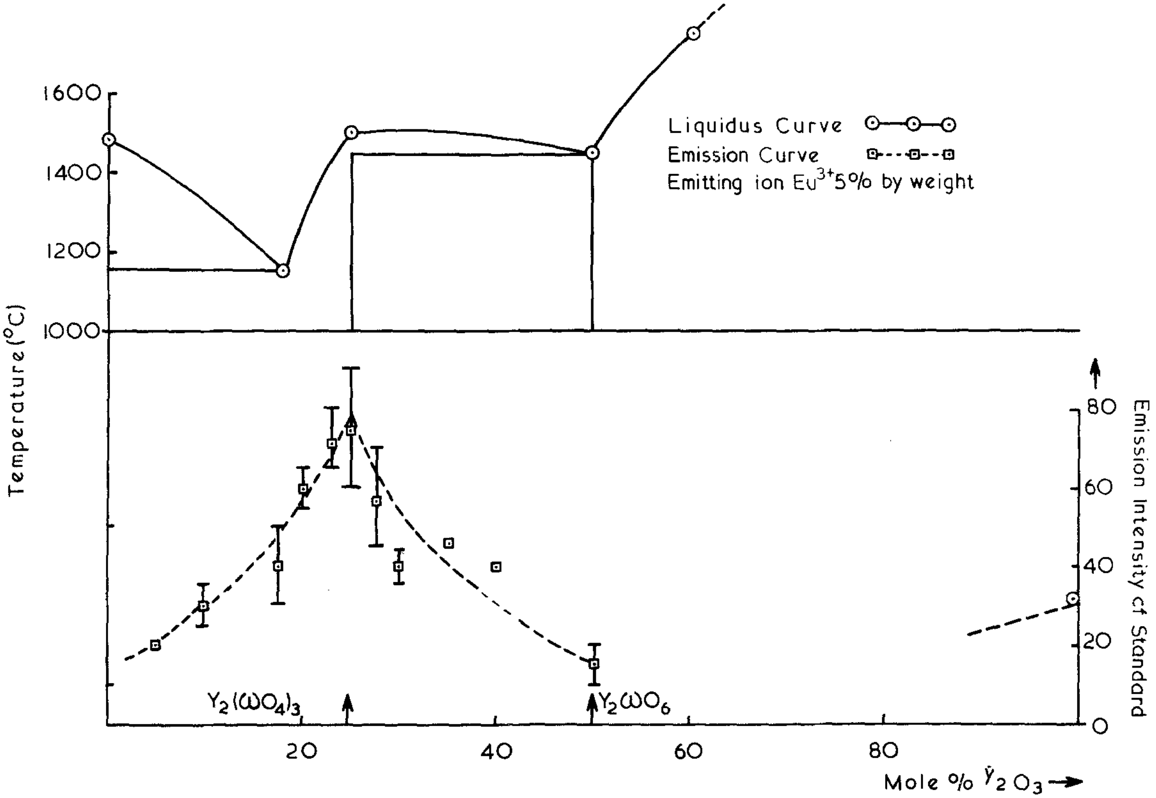

Figure 1 Emission intensity (Eu^{3+}) as a function of composition in the Y$_2$O$_3$–WO$_3$ phase system.

be concluded that the concentrations of lattice emitting centres in the oxytungstate is not high and that such centres are not necessarily tungstate ions, since these are in abundance in the lattice. The results of reduction by hydgrogen (Tables I and II) show that the lattice emission is not greatly affected but that the Eu^{3+} emission is affected. The latter is also true of the normal tungstate. Lattice emission is hence not necessarily related to reduced-valency tungstate ions inadvertently present in the hosts since these might be expected to increase with preparation in reducing atmospheres, even though the compounds are of different structures, i.e., normal tungstate is rhombohedral [6], oxytungstate is monoclinic [7]. Again, on the basis of the simplest model, at a 10% doping level there is only one europium tungstate molecule for every one hundred molecules of yttrium tungstate. Thus, as stated, there are adequate yttrium oxytungstate molecules available to emit.

It is concluded that lattice emission arose from structural defects in the phosphor crystallites such as dislocations, microcracks, slip systems and crystal grain boundaries. Such centres are distortions in the lattice and have associated electric fields. Even a very simplistic model about dislocations leads to the conclusion that about 10^{14} atoms could be missing from one cubic centimetre of crystal. Since dopants often accumulate at such points in crystals during growth, the Eu^{3+} ions are in this case assumed to do the same, blocking the defect emission.

Acknowledgement

This paper is published by permission of the © Controller HM Stationery Office, London.

References

1. H. J. BORCHARDT, *Inorg. Chem.* 2 (1962).
2. *Idem*, *J. Chem. Phys* 39 (1963) 504.
3. L. G. VAN UITERT, *J. Electrochem. Soc.* **110** (1963) 46.
4. K. NASSAU, H. J. LEVINSTEIN, G. M. LOIACANO, *J. Chem. Phys. Sol.* **26** (1965) 1805.

5. G. BLASSE, A. BRIL, *J. Chem. Phys.* **45** (1966) 2350.
6. O. BEAURY, M. FAUCHER, P. CARO, *Mater. Res. Bull.* **13** (1978) 175.
7. G. BLASSE. *J. Inorg. Nucl. Chem.* 28 (1966(1488.

Received 12 January
and accepted 9 April 1981

D. S. ROBERTSON
P. W. SMITH
Royal Signals and Radar Establishment,
St. Andrews Road,
Great Malvern,
Worcs.,
UK