only the basal faces of the crystals were well-formed and with few growth features; the usual trigonal habit was poorly developed. To achieve even minimal transport along the ampoule the reaction temperature had to be raised above 1000° C for a growth time of 1000 h. The distance over which transport then occurred was never greater than 3 cm. At lower growth temperatures transport did not occur, but a mass of small intergrown crystals formed on the untransported charge. The slow rates of transport achieved are thought to be caused by a low reaction rate between the iodine transporter and the hafnium used, which was in the form of wire.

Small crystals of hafnium diselenide were grown similarly. By varying the Se:Hf ratio in the charge, diselenide crystals varying in composition from Se:Hf :: 1.98 ± 0.03 to Se:Hf :: 1.92 ± 0.03 were obtained. The growth products were metallic bronze in colour, with well-developed faces and edges. Crystals were transported a distance of 5 cm from the charge under the conditions quoted, but were often intergrown.

Single crystals of three compositions of solid solutions in the series HfS_xSe_{2-x} ($0 \leqslant x \leqslant 2$) were grown. These varied in colour from transparent orange-red (sulphur-rich) to metallic bronze (selenium-rich). All solutions formed a single phase trigonal compound isomorphous with the disulphide and diselenide. X-ray powder data have been used to derive the unit cell dimensions listed in Table II. Cell axial lengths are almost linear functions of the composition variable, x, but slight quadratic deviations from linearity appear in the "c" dimension.

The oxide reduction technique showed the single crystal growth products to be close in composition to that of the mix of elements forming the original charge. Results of analyses are given in Table III.

TABLE III Compositions of solid solutions as determined by the oxide reduction technique

Compound	Sulphur fraction	Selenium fraction
$HfS_{1.5}Se_{0.5}$	1.52 ± 0.03	0.48 ± 0.03
$HfS_{1.0}Se_{1.0}$	1.03 ± 0.03	0.97 ± 0.03
$HfS_{0.5}Se_{1.5}$	0.51 ± 0.03	1.49 ± 0.03

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On the methods for determining trap depth from glow curves

In a recent paper, Shalgaonkar and Narlikar [1] review some of the important methods used in the determination of trap depth from glow curves. The purpose of the present note is threefold:

1. suggesting the possibility of using the mentioned methods in their more modern versions which enable more accurate evaluation of the activation energies by simpler and more direct calculation;
2. pointing out the differences between thermally stimulated conductivity (TSC) and thermally stimulated luminescence (TSL) (usually called thermoluminescence, TL). In addition, a few more phenomena can be included in this category, for which the determination of activation energies is both relevant and important;
3. a few possible errors in the paper of Shalgaonkar and Narlikar are to be corrected.

The method of various heating rates due to Hoogenstraaten [2] mentioned in [1] has been generalized [3] in two ways. First, it has been shown that the method is applicable when non-linear heating rates are used, namely, that a straight line with a slope of E/k is expected when plotting $\ln(T_m{}^2/\beta_m)$ versus $(1/T_m)$ where $T_m(K)$ is the temperature of the glow maximum and β_m(K sec^{-1}) is the instantaneous heating rate at the maximum. E is the activation energy (eV) and k is Boltzmann's constant (eV K^{-1}). Secondly, Chen and Winer [3] showed that this method is applicable not only to first order glow peaks but also to second order or "general" order peaks, i.e. curves obeying the equation [4]

$$I = -a\,\mathrm{d}m/\mathrm{d}t = Am^{\alpha}\exp(-E/kT) \quad (1)$$

where α is the kinetics order, not necessarily 1 or 2, a and A are constants, and m is the concentration of trapped carriers at depth E.

It is also to be mentioned that the "initial rise" method [5] is applicable to the general order case and not only to first and second order cases as mentioned by Shalgaonkar and Narlikar [1].

The method of Halperin and Braner [6] as given in Equations 22 and 23 [1] has the disadvantage that E has to be evaluated in an iterative manner. One has to estimate E assuming $\Delta = 0$, then calculate $\Delta = 2kT_m/E$, and then re-evaluate E. Chen [7] suggested a correction to this method which includes equations which are more accurate and non-iterative. For first order, the equation is now

$$E_1 = 1.52\,kT_m{}^2/(T_m - T_1) - (1.58 \times 2kT_m) \quad (2)$$

and for second order kinetics

$$E_2 = 1.81\,kT_m{}^2/(T_m - T_1) - 2\,kT_m\,, \quad (3)$$

where T_1 and T_2 are the low and high temperatures of half maximum intensity. Chen [7] has also discussed the relative merits of methods based on the total half width of the glow peak, $T_2 - T_1$, the low temperature half width $T_m - T_1$ and the high temperature one $T_2 - T_m$. Equations 2 and 3 are related to the case of temperature independent frequency factors s(sec^{-1}). If s depends on the temperature as T^P, it has been shown [7] that the proper correction to Equations 2 and 3 and to Lushchik's [8] method is by subtracting $P\ kT_m$ from the value otherwise obtained. It is to be noted that Equations 22 and 23 in [1] are also related to the case of $s \propto T^P$ with $P = 2$.

The "form factor" $\mu_g = (T_2 - T_m)/(T_2 - T_1)$ introduced by Halperin and Braner [6] has also been discussed by Chen [7] who showed that $\mu_g \approx 0.42$ is characteristic to first order peaks and $\mu_g \approx 0.52$ to second order ones. The value of μ_g was also used [9] as a parameter aiding the evaluation of trap depth in cases of general order kinetics. This was done after a correlation had been found between the form factor μ_g and the order of kinetics α [9]. More recent methods of curve fitting for evaluating glow parameters are also to be mentioned here [10-12].

Shalgaonkar and Narlikar [1], following other investigators, proposed the study of TSL and TSC peaks by the same methods. It is important to note that the mentioned methods were primarily developed for TSL peaks and only later used for TSC. The relation between the conductivity σ and the TSL intensity I, is $\sigma = \tau e \mu I$ where τ is the lifetime of the charge carrier in the conduction band, e the electronic charge and μ the mobility. Thus, the temperature dependence of τ and μ should be taken into account. The latter is known to be slightly temperature dependent, which can usually be disregarded as long as a not too broad temperature range is considered. Saunders [13] showed that the assumption that the lifetime τ is constant, is not necessarily true. His case of TSC corresponding to second order TSL was further developed [14] and the TSC curve was shown to substantially vary from its TSL counterpart. Thus, the methods for evaluating the activation energy (other than the initial rise method) from TSL curves are not necessarily applicable to the TSC curves and new methods were developed [14]. A similar procedure was taken for TSC peaks corresponding to first order TSL curves with non-constant τ [15, 16].

A few more phenomena obey the same equations as those of TSL and, therefore, can be analysed by the same methods. In all these cases there is an "activation energy" which is an important parameter. One of these phenomena is thermally stimulated electron emission (TSEE) [17] which is the release of thermally stimulated electrons from a crystal in vacuum. This method is closely related to the TSC with the exceptions that the dependence of the mobility on temperature should not be taken into account and that only peaks due to the release of electrons (and not holes) can appear. Another similar technique is the ionic thermal conductivity (ITC) [18] sometimes called thermal depolarization) in which one usually has first order peaks. Other phenomena which can be analysed by these methods are thermal desorption curves [19] and thermogravimetry [20].

Finally, a few corrections are to be made to

Shalgaonkar and Narlikar's review paper as follows:

(a) the curve in Fig. 1 [1] is by no means a typical single glow peak. The form factor μ_g in the given curve is about 0.6 whereas, as mentioned above, a typical value for first order curves is ~0.42 and for second order ~0.52. The above mentioned TSC peaks corresponding to second order TSL have very high values of the form factor, namely, $\mu_g \sim 0.8$ [14] whereas those corresponding to first order have $\mu_g < 0.4$ [15]. Thus, the shape of the curve in Fig. 1 does not correspond to any known single glow curve;

(b) a minus sign in missing in Equation 1 which should read $-\mathrm{d}n/\mathrm{d}t = ns\exp[-E/kT]$;

(c) the expression of q_1 following Equation 21 should read [6] $q_1 = [1.72\ \mu_g/(1 - \mu_g)](1 - 1.58\Delta)$. The definition of μ_g should be $\mu_g = (T_2 - T_m)/(T_2 - T_1)$;

(d) Equation 24 should read [7] $E_1 = 2kT_m[1.25\,T_m/(T_2 - T_1) - 1]$, and Equation 25 should read $E_2 = 2kT_m[1.77\,T_m/(T_2 - T_1) - 1]$;

(e) following Equation 26, the definition of Γ should be $\Gamma = (T_2 - T_m)/(T_m - T_1)$;

(f) in the method proposed by Muntoni *et al* [4], one should distinguish between two constants, a and α. Thus, Equation 28 should read $-\mathrm{d}m/\mathrm{d}t = Am^{\alpha}\exp(-E/kT); I = -a\beta(\mathrm{d}m/\mathrm{d}T)$. Following Equation 29, the constant C should be defined as $C = \log(Aa^{1-\alpha}\beta^{\alpha})$.

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