

# The identification of the reaction mechanism in rising temperature kinetic studies based on the shape of the DTG curve

Yoke Foo Lee, David Dollimore\*

*The Department of Chemistry and College of Pharmacy, The University of Toledo, Toledo, OH 43606, USA*

Received 5 May 1998; received in revised form 20 July 1998; accepted 22 July 1998

---

## Abstract

A method of identifying the kinetic mechanism based on the shape or asymmetry of TG and DTG curves is outlined. The asymmetry is described, both qualitatively and quantitatively. The qualitative approach separates the various kinetic equations into three groups by their characteristic onset and final temperatures. The quantitative approach utilizes parameters such as  $\alpha_{\max}$  and half-width pertaining to the DTG curve. Examples of selecting the appropriate kinetic equation using the proposed methods are given. © 1998 Elsevier Science B.V. All rights reserved.

*Keywords:* Kinetic analysis; Computer models; Thermogravimetry

---

## 1. Introduction

One of the challenges of rising temperature solid-state kinetic studies is to identify a kinetic equation, which describes the reaction of the system under study. The various equations can take different forms depending on the reaction occurring, and the commonly encountered mechanisms have been summarized by Keatch and Dollimore [1] and by Brown [2].

Many methods [3,4] have been proposed to meet this challenge. One common setback of these methods is that a decision can only be made after scanning all the possible equations. Alternatively, one can perform a single isothermal experiment and determine the kinetic mechanism by the established method of Jones et al. [5] or Sharp et al. [6]. However, the kinetics of constant temperature experiment may not apply to rising temperature decomposition. A relatively simple

method is proposed to select the appropriate kinetic mechanism based on the asymmetry or shape of the DTG curve.

## 2. Kinetic analysis of TG curves

The characteristic shape of TG and, hence, DTG traces are kinetically dependent [7,8]. It is envisaged that the shape of these curves may be used to identify the kinetic expression to describe the behavior of solid-state decompositions.

A computer program [9], using the differential form of these relationships based on the finite difference method, allowed  $\alpha$  (fraction decomposed)–temperature plots to be developed, given the Arrhenius parameters ( $A$  and  $E$ ), the kinetics equation and the heating rate. Using this program, a systematic theoretical study has been performed; three variables are kept constant while the fourth variable is changed and its

---

\*Corresponding author.

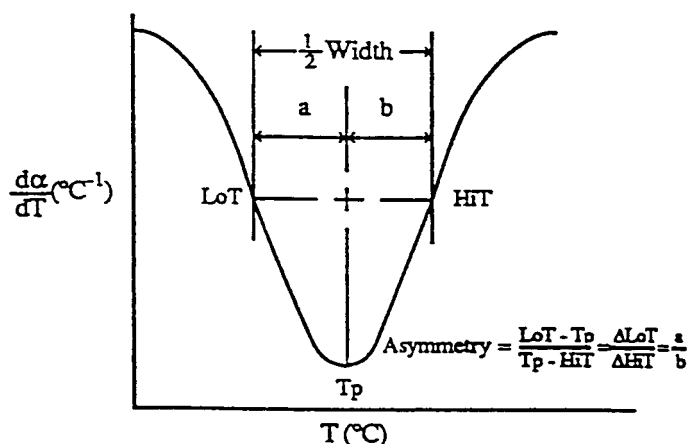


Fig. 1. A schematic DTG plot and the terminology used to describe the shape.

effects on the TG and DTG traces are noted. Fig. 1 explains the terminology used here to describe the shape of the DTG plot.  $T_p$  represents the peak temperature, where  $d\alpha/dT$  is at its maximum. The half-width represents the width at half peak height.

The higher and lower temperature ends of the half-width are represented by HiT and LoT, respectively. The ratio  $a/b$  is termed the asymmetry or shape factor. Alternatively,  $a/b$  can be calculated by  $\Delta LoT/\Delta HiT$  or  $(T_p - LoT)/(HiT - T_p)$ . For a symmetric curve, the ratio equals unity, and any deviation measures the asymmetry of the curve.

From the results of the theoretical exercise, it is apparent that the 'sharpness' of the onset and final temperatures are due to kinetic factors – especially the

kinetic mechanism. Certain kinetic expressions lead to an asymptotic or 'diffuse' departure from the base line in a DTG plot, while others produce a very 'sharp' approach to the final plateau. Table 1 lists the various theoretical parameters pertaining to the DTG curve obtained at  $A = 1.0 \times 10^{15} \text{ s}^{-1}$ , and  $E = 210 \text{ kJ/mol}$  and heating rate  $= 10^\circ\text{C/min}$ . An inspection of Table 1 (paying attention to  $\Delta LoT/\Delta HiT$ ) and of published plots of  $d\alpha/dT$  against temperature [10] establishes the following facts regarding mechanism and  $T_i$  (onset or initial temperature) and  $T_f$  (final temperature).

The mechanisms  $A_2$ ,  $A_3$ , and  $A_4$  have both  $T_i$  and  $T_f$  sharp ( $\Delta LoT/\Delta HiT = 1$ ). The curves with  $T_i$  and  $T_f$  sharp include mechanisms  $R_2$ ,  $R_3$ ,  $D_1$ ,  $D_2$ ,  $D_3$ , and  $D_4$ . These curves have  $\Delta LoT/\Delta HiT \gg 1$ . Kinetic equa-

Table 1

Reconstructed thermal analysis data for  $E = 210 \text{ kJ/mol}$ ,  $A = 1.0 \times 10^{15} \text{ s}^{-1}$  and heating rate  $5^\circ\text{C/min}$  as a function of half-width and shape factors for various mechanisms

Rkn Mech	Half-width (HiT–LoT) $^\circ\text{C}$	$T_p$ $^\circ\text{C}$	Lo $^\circ\text{C}$	HiT $^\circ\text{C}$	$\Delta LoT/\Delta HiT$
A <sub>2</sub>	18.0	358.9	350.0	368.0	0.09
A <sub>3</sub>	12.0	358.8	352.0	364.0	1.31
A <sub>4</sub>	9.99	358.3	354.0	364.0	0.754
R <sub>2</sub>	26.0	348.4	332.0	358.0	1.71
R <sub>3</sub>	30.0	342.4	324.0	354.0	1.59
D <sub>1</sub>	22.0	359.1	338.0	360.0	23.4
D <sub>2</sub>	44.0	348.8	316.0	360.0	2.93
D <sub>3</sub>	58.0	325.7	290.0	348.0	1.60
D <sub>4</sub>	48.0	326.6	294.0	342.0	2.12
F <sub>1</sub>	36.0	358.4	338.0	374.0	1.31
F <sub>2</sub>	54.0	357.7	332.0	386.0	0.91
F <sub>3</sub>	68.0	367.6	340.0	408.0	0.68

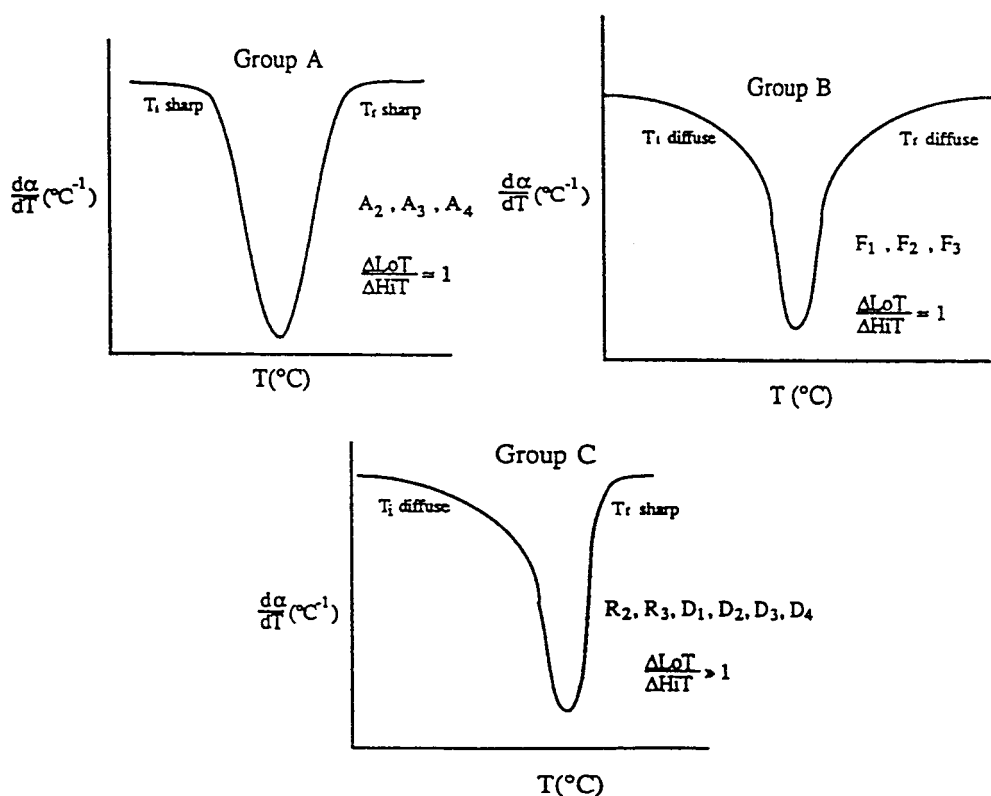


Fig. 2. Schematic DTG traces showing the characteristics.

tions  $F_1$ ,  $F_2$  and  $F_3$  belong to the group, where both  $T_i$  and  $T_f$  are diffuse; here,  $\Delta L_oT/\Delta H_iT \approx 1$ . Fig. 2 shows the schematic plots. One can, therefore, by a visual inspection of the DTG trace, narrow down the possible mechanism. For instance, if a DTG plot has a slow departure and a fast return to the base line, one can probably ignore the Avrami–Erofeev and first-order equations.

To further discern the equations within a group, one needs to look at the half-width and associated parameters connected with the asymmetry of the curve. It is shown [11] that  $\alpha_{max}$ , which is the fraction decomposed at maximum rate and half-width, can help to further characterize the mechanism. Table 2 summarizes these data for all the mechanisms examined. It is observed that  $\alpha_{max}$  does not change appreciably over a wide range of Arrhenius parameters and heating rates. However, the half-width spans over a wider range. Therefore, based on the shape of the DTG curve coupled with  $\alpha_{max}$  and half-

width, a method is developed to identify the kinetic mechanism.

### 3. Methodology

The program used in the kinetic analysis of the examples cited is written in FOXPRO, based on the original computer program [9] written in BASIC. However, additional features, such as the selection of the kinetic mechanism and the computation of the Arrhenius parameters, are incorporated into the program.

A flow chart of the method for identifying the mechanism is given in Fig. 3. At the start, the data of % weight loss and temperature at  $1^\circ\text{C}$  interval are obtained from the TG work station. A small temperature interval is desired as it gives better accuracy in determining the various parameters pertaining to the DTG curve. These data are input to the computer,

Table 2  
Reasonable limits of  $\alpha_{\max}$  and half-width for various mechanisms obtained from theoretical study

Mechanism	$\alpha_{\max}$ Range	Half-width
P <sub>1</sub>	1.00	<12.00
A <sub>2</sub>	0.62–0.63	14–32
A <sub>3</sub>	0.63	12–22
A <sub>4</sub>	0.63–0.65	<10.00
B <sub>1</sub>	0.54–0.55	8–12
R <sub>2</sub>	0.73–0.74	24–34
R <sub>3</sub>	0.69	20–42
D <sub>1</sub>	1.00	24.00
D <sub>2</sub>	0.81–0.82	24–78
D <sub>3</sub>	0.67–0.68	30–70
D <sub>4</sub>	0.75–0.76	38–80
F <sub>1</sub>	0.62	20–60
F <sub>2</sub>	0.48	22–94
F <sub>3</sub>	0.40	>66.00

which converts the % weight loss to  $\alpha$  values. The experimental  $\alpha_{\max}$ , HiT, LoT and half-width are determined. The program then narrows down the possible equations by comparing the experimental  $\alpha_{\max}$  to the theoretical  $\alpha_{\max}$  range. It is observed that D<sub>2</sub> and B<sub>1</sub>

can be identified based on the  $\alpha_{\max}$  alone. Both F<sub>2</sub> and F<sub>3</sub> cannot be further separated based on the half-width and shape factor. However, the other mechanisms may be further separated. At this point, the computer will prompt the user for the shape factor, i.e. whether T<sub>i</sub> and T<sub>f</sub> are diffuse or sharp. This can easily be discerned from the DTG plot obtained from the TG work station.

In the  $0.9 \leq \alpha_{\max} \leq 1.0$  range, D<sub>1</sub> can be discriminated by the shape factor alone. R<sub>2</sub> and D<sub>4</sub> can be separated by the half-width, and in the  $0.6 \leq \alpha_{\max} < 0.7$  range, the first-order equation can be distinguished from the Arvami–Erofeev equations and D<sub>3</sub>/R<sub>3</sub>, based on the shape factor. Subsequently, the other equations can be individually identified, based on half-width.

In the event, when there is an overlapping of half-width between two equations, the program will recommend both equations. If the experimental half-width falls beyond the range stipulated, the recommendation is based on  $\alpha_{\max}$  and/or shape factor. The kinetic equation once identified will be used to calculate the specific rate constant ( $k$ ) by the following:

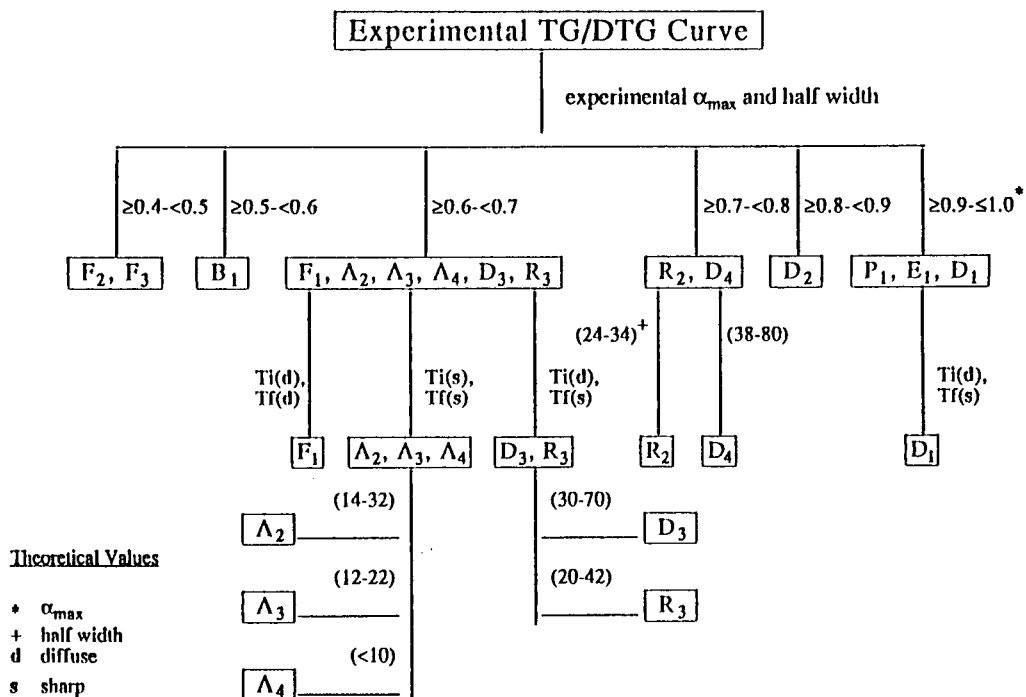


Fig. 3. Flow chart showing the procedures in recognizing the kinetic equations.

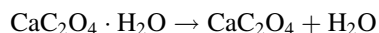
$$k = \frac{(d\alpha/dT)\beta}{f(\alpha)} = A \exp\left(\frac{-E}{RT}\right) \quad (1)$$

where  $d\alpha/dT$  is the fraction decomposed per degree,  $\beta$  the heating rate ( $^{\circ}\text{C/s}$ ),  $f(\alpha)$  the differential form of the kinetic equation and  $R$  the gas constant. The activation energy and the pre-exponential factor can be calculated from an Arrhenius plot of  $\ln k$  vs.  $T^{-1}$ . The Arrhenius parameters, together with the heating rate and kinetic equation, are used to reconstruct the experimental TG and DTG curves. The theoretical parameters, i.e.  $\alpha_{\max}$ ,  $T_p$ , LoT, HiT, half-width describing the asymmetry of the DTG curve are then compared to the values obtained experimentally. A close match indicates a correct choice of the kinetic equation.

Two examples of mechanism identification based on the foregoing methodology are given. These

include the dehydration of calcium oxalate monohydrate and the decomposition of limestone. All experiments are performed with a DuPont 1090 work station coupled to a TG 951 furnace.

(1) Dehydration of calcium oxalate monohydrate:



The various experimental parameters pertaining to the DTG curve are given in Table 3(a). From Fig. 4 it is observed that this plot belongs to the group which has  $T_i$  diffuse and  $T_f$  sharp. Also,  $d\alpha/dT$  is larger than unity, which is consistent with the theoretical study. Following the flow chart and based on the experimental  $\alpha_{\max}$  alone,  $R_2$  and  $D_4$  equations are favored. Since both,  $R_w$  and  $D_4$  equations have the same characteristic shape factor, i.e.  $T_i$  diffuse and  $T_f$  sharp, further separation between these two equations are based on their half-widths. The experimental half-

Table 3

Parameters describing the asymmetry of the DTG curve for the dehydration of calcium oxalate monohydrate at  $20^{\circ}\text{C}/\text{min}$  in air

$\alpha_{\max}$	$T_p$ $^{\circ}\text{C}$	LoT $^{\circ}\text{C}$	HiT $^{\circ}\text{C}$	Half-width	$\Delta\text{LoT}/\Delta\text{HiT}$	$T_i$	$T_f$
(a) <i>Experimental</i>							
0.787	237.2	198.7	251.0	52.3	2.79	diffuse	sharp
(b) <i>Theoretical</i>							
Mechanism	$\alpha_{\max}$	$T_p$ $^{\circ}\text{C}$	LoT $^{\circ}\text{C}$	HiT $^{\circ}\text{C}$	Half-width $^{\circ}\text{C}$		
$R_s$	0.718	214.8	177	234	65		
$D_4$	0.748	237.7	205	255	50		

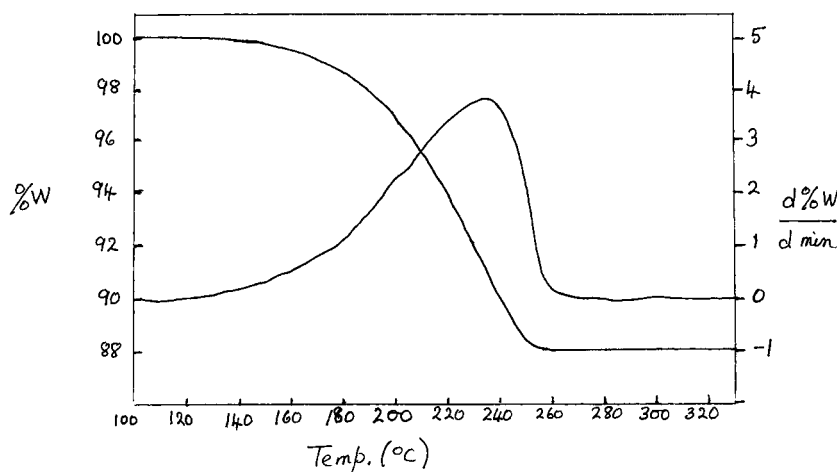


Fig. 4. TG and DTG curves for the dehydration of calcium oxalate monohydrate at  $20^{\circ}\text{C}/\text{min}$  in dynamic air.

Table 4

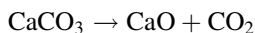
Parameters describing the asymmetry of the DTG curve for the decomposition of limestone at 10°C/min in air

$\alpha_{\max}$	$T_p$ °C	LoT °C	HiT °C	Half-width	$\Delta\text{LoT}/\Delta\text{HiT}$	$T_i$	$T_f$
(a) <i>Experimental</i> 0.678	814.2	757.4	845.4	88.0	1.82	diffuse	sharp
(b) <i>Theoretical</i> Mechanism	$\alpha_{\max}$	$T_p$ °C	LoT °C	HiT °C	Half-width °C		
R <sub>3</sub>	0.673	817.9	762.0	851.0	89.0		
D <sub>3</sub>	0.682	818.7	670.0	819.0	149.0		

width is 52.3°C, which is an indication that D<sub>4</sub> mechanism is more favored.

For a comparison, both the Arrhenius parameters for R<sub>2</sub> and D<sub>4</sub> were used to reconstruct the experimental TG curve. Table 3(b) shows the theoretical parameters obtained. When one compares the theoretical and experimental parameters, D<sub>4</sub> mechanism with activation energy of 143.3 kJ/mol and a pre-exponential factor of  $9.31 \times 10^{11} \text{ s}^{-1}$ .

#### (2) Decomposition of limestone



The experimental parameters are given in Table 4(a). A glance at Fig. 5 shows that  $T_i$  is diffuse and  $T_f$  sharp. Again, following the flow chart, the possible mechanism from the experimental  $\alpha_{\max}$  are F<sub>1</sub>, A<sub>2</sub>, A<sub>3</sub>, D<sub>3</sub> and R<sub>3</sub>. Since the curve has  $T_i$  diffuse and  $T_f$  sharp, the Avrami–Erofeev and the first-order

equations are disregarded. However, in this case, the experimental half-width (88.0°C) is not within the theoretical range, thus further separation between these two equations is not feasible and the program recommends both, D<sub>3</sub> and R<sub>3</sub> as the possible mechanism. From Table 4(b), the R<sub>3</sub> mechanism is a better choice to describe the decomposition. The Arrhenius parameters obtained are  $E=205.7 \text{ kJ/mol}$  and  $A=8.41 \times 10^6 \text{ s}^{-1}$ .

#### 4. Conclusion

A method is described to select the kinetic mechanism based on the asymmetry of the DTG curve. The main advantage of this method is shown by the two examples cited. A cursory inspection of the shape of the curve will narrow down the number of possible

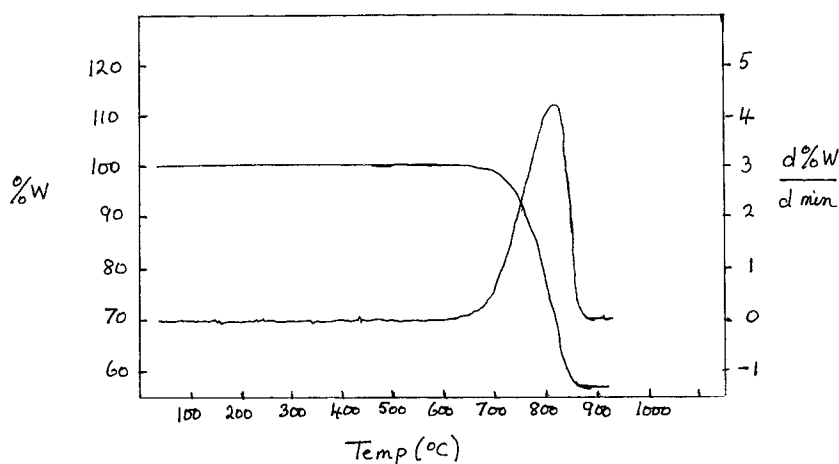


Fig. 5. TG and DTG plots for the decomposition of limestone at 10°C/min in dynamic air.

equations for consideration. In addition, the various parameters describing the DTG curve can be obtained easily without extensive computation.

## References

- [1] C.J. Keatch, D. Dollimore, *An Introduction to Thermogravimetry*, 2nd edn., Heyden, London, 1975.
- [2] M.E. Brown, *Introduction to Thermal Analysis*, Chapman and Hall, London, 1988, pp. 131.
- [3] A.W. Coats, J.P. Redfern, *Nature (London)* 201 (1964) 68.
- [4] V. Satava, *Thermochim. Acta* 2 (1971) 423.
- [5] L.F. Jones, D. Dollimore, T. Nicklin, *Thermochim. Acta* 13 (1975) 240.
- [6] J.H. Sharp, G.W. Brindley, B.N.N. Achar, *J. Am. Ceram. Soc.* 49 (1966) 379.
- [7] J. Sestek, V. Satava, W.W. Wendlandt, *Thermochim. Acta* 7 (1973) 333.
- [8] G. Varhegyi, T. Szekely, *Thermochim. Acta* 57 (1982) 13.
- [9] D. Dollimore, T.A. Evans, Y.F. Lee, F.W. Wilburn, *Thermochim. Acta* 1988 (1991) 77.
- [10] M.E. Brown, D. Dollimore, A.K. Galwey, *Reactions in the Solid State*, C.H. Bamford and C.F.H. Tippers (Eds.), *Chemical Kinetics*, Vol. 22, Elsevier, Amsterdam, 1980, pp. 340.
- [11] D. Dollimore, T.A. Evans, Y.F. Lee, F.W. Wilburn, *NATAS Proceedings*, 1990, 2, pp. 397.