

## LEAD SILICATE-POTASSIUM CARBONATE SOLID-SOLID REACTION KINETICS

B. K. SPERONELLO, C. J. BRINKER AND W. R. JTT

*Department of Ceramics, Rutgers - The State University of New Jersey, New Brunswick, N.J. 08903  
(U. S. A.)*

(Received 17 August 1972)

### ABSTRACT

The kinetics and mechanism of the reaction between  $4\text{PbO}\cdot\text{SiO}_2 + \text{K}_2\text{CO}_3$  and  $\text{PbO}\cdot\text{SiO}_2 + \text{K}_2\text{CO}_3$  were studied using isothermal weight change determinations and thermal gravimetry (TG) to monitor the fraction of the reaction completed as a function of time. The reactions were found to be nuclei growth controlled with one-dimensional diffusion controlled growth having procedural activation energies of 85 and 108 kcal/mole respectively.

The results from the TG methods of Test, Weidemann and Vaughan and Sativa were compared with the isothermal data to determine their relative merits. These methods were found to be, with reservations, suitable for determining the procedural activation energy. However, the method of Sativa was found to be lacking in sufficient sensitivity to allow determination of the reaction mechanism.

### INTRODUCTION

The kinetics and mechanism of the reactions between potassium carbonate and  $4\text{PbO}\cdot\text{SiO}_2$  and potassium carbonate and  $\text{PbO}\cdot\text{SiO}_2$  were studied by: 1) inert markers to indicate the diffusing species, 2) X-ray diffraction to determine the reaction products, 3) the electron microprobe to determine the distribution of product and reactant phases, and 4) isothermal weight change determinations to establish the fraction of the reaction completed as a function of time. These data were used to determine the reaction mechanism, rate constants and the procedural activation energy.

Thermogravimetric (TG) studies were made using the methods of analysis of Tets, Weidemann and Vaughan<sup>1</sup> and Sativa<sup>2</sup>. These results were compared with those obtained from the isothermal experiments and the TG techniques were compared and evaluated.

### THEORETICAL CONSIDERATIONS

The rate of product formation in additive solid-solid reactions is governed by either: 1) the diffusion of reactants through a continuous product layer, 2) nucleation of the product at active sites and growth of the nucleated particles, or 3) phase boundary reactions. The rate of reaction is dependent on the slowest of these steps. For

each of these mechanisms a number of models have been proposed. The mathematical models of Jander<sup>3</sup>, Ginstling and Brounstein<sup>4</sup>, and others<sup>5</sup> have all been suggested for diffusion controlled reactions. Each of these models varies in the initial assumptions used in the derivation. Several models have been proposed for phase boundary controlled reactions. These vary in the geometry of the initial particle and shape of the contracting envelope, but all are based on the interfacial area available for reaction. The nuclei growth equation is of the general form:  $-\ln(1-x) = Kt^m$  where  $x$  is the fraction of the reaction completed at time  $t$ .  $K$  is the rate constant and  $m$  is a parameter which is a function of: 1) reaction mechanism, 2) nucleation rate, and 3) geometry of the nuclei. By establishing a value for  $m$ , the growth habit can be inferred: although the value is not necessarily unique and hence the results are not conclusive. Values of  $m$  tabulated by Hulbert<sup>5</sup> for various boundary conditions were used to deduce the growth habit.

In addition to these three mechanisms, attempts have been made to relate solid-solid reaction kinetics to the concept of the ordered reaction. Only one value of  $n$ , the reaction order, has unique significance. When the rate determining step is the nucleation process and an equal probability of nucleation at each site exists,  $n$  is equal to one.

The rate equations and the assumptions used in deriving them are given by Hulbert<sup>5</sup>. A model is assumed to be correct if the reaction rate constant is independent of time under isothermal conditions. The rate constants in most of the reaction kinetic models mentioned are a function of the diffusion constant. When this is the case, an Arrhenius plot can be used to determine the procedural activation energy of the reaction<sup>6</sup>.

Normally the activation energy must be calculated indirectly from the rate equations and constants. The method of Tets, Weidemann and Vaughan<sup>1</sup> allows this to be determined directly from TG data at any stage with a plot of the inverse of the absolute temperature versus the natural logarithm of the reaction rate at a constant fraction of reaction.

The TG method of Sativa<sup>2</sup> postulates that for a constant rate of temperature increase,  $\ln g(x) - \ln p(x) = B$  where  $g(x)$  is dependent upon the reaction mechanism,  $B$  is a constant, and  $p(x)$  is to a first approximation a linear function of the inverse of the absolute temperature. If  $\ln p(x)$  is plotted against  $1/T$  °K the result will be linear for the correct mechanism, and from the slope of the plot the activation energy may be calculated.

## EXPERIMENTAL

The  $4\text{PbO}\cdot\text{SiO}_2$  and  $\text{PbO}\cdot\text{SiO}_2$  were prepared by heating Ottawa powdered Flint and Hammond Lead Products Litharge at 690 and 740°C respectively, for 72 hours. The samples were crushed and blended after each 24 hours of heat treatment. X-ray diffraction established the phase present. The potassium carbonate is Hooker Chemical Co.'s calcined carbonate of potash. Prior to use both materials were dried

24 hours at 150°C. Particle size fractions were obtained by using an Allan Bradley Sonic Sifter.

The Mettler Thermoanalyzer was used to obtain the isothermal weight change determinations and TG data. The samples were weighed, blended and vibrated in an 8 mm Pt macro crucible. They were dried at 150°C in the thermoanalyzer for 2 hours and brought to temperature at 15°C/min for the isothermal experiments or at 4, 2, 1 or ½°C/min for the TG experiments. The isothermal experiments to determine the effect of lead metasilicate particle size were made at 575°C. An air atmosphere, forced through molecular sieve material to remove the moisture, was passed over the sample at a rate of 5.7 l/h.

Inert platinum marker experiments were used to establish the species diffusing during the reaction. The experimental technique followed the method described by Carter<sup>7</sup>. Sections of 0.001 inch Pt wire were placed between pressed pellets and the specimens were heat treated at 650°C.

Standard qualitative X-ray diffraction techniques were used to identify the reaction products. The electron microprobe was used to establish the distribution of the product phase with respect to the reactants. Electron backscatter data and X-ray emission scans for Pb, K and Si were obtained from samples of each reaction.

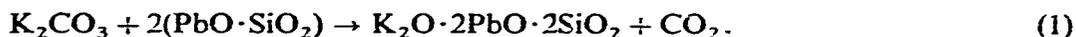
## RESULTS AND DISCUSSION

### A. $PbO \cdot SiO_2$ and $K_2CO_3$ reaction

After heating, the inert markers placed between the lead metasilicate and potassium carbonate pellets were at the potassium carbonate-product interface, indicating there was one way transfer of  $K_2O$  as either ions or molecules.

Isothermal experiments were run at 550–650°C in 25°C increments. Above 650°C the presence of a liquid phase was possible<sup>8</sup>.

X-ray diffraction analysis of the partially reacted and completely reacted samples established  $K_2O \cdot 2PbO \cdot 2SiO_2$  as the product phase. Hence the reaction may be represented as



From data establishing the fraction of the reaction completed as a function of time the various solid–solid reaction kinetic models can be examined. In all cases the model is assumed correct if the reaction constant ( $K$ ) is independent of time ( $t$ ). Thus a plot of  $K$  versus  $t$  should result in a horizontal line for the correct model. This plot is shown in Fig. 1. From this data it is clear that only the nuclei growth model demonstrates the independence of  $K$  from  $t$ .

From the general form of the equation for the nuclei growth model the rate constant ( $K$ ) and the exponent  $m$  can be determined from a plot of  $\ln 1/(1-x)$  versus  $\ln t$ . The slope is  $m$  and the intercept  $m \ln k$ . This data is shown in Fig. 2 and it is evident that  $m = \frac{1}{2}$ . This value of  $m$  implies the growth is one dimensional and diffusion controlled with a zero or decreasing nucleation rate.

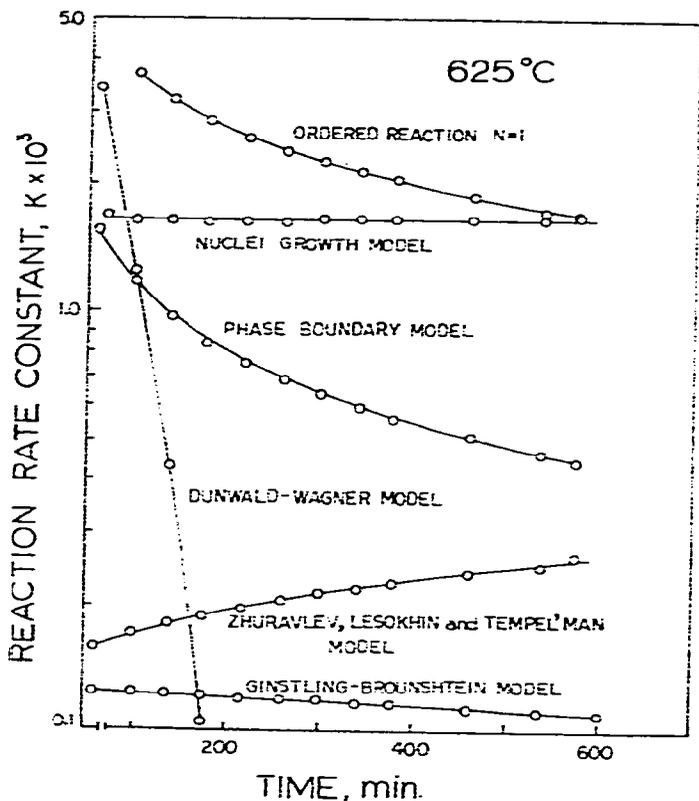


Fig. 1. Analysis of reaction rate equations for the  $K_2CO_3 + PbO \cdot SiO_2$  reaction.

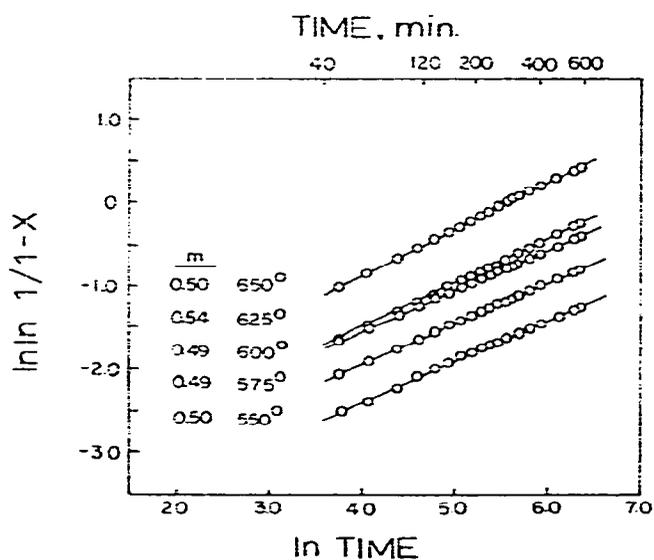


Fig. 2. Nuclei growth model for the  $K_2CO_3 + PbO \cdot SiO_2$  reaction.

To show the effect of surface area on the rate, experiments were performed in which the lead metasilicate particle size was increased. Increasing the particle size ( $r$ ) for a particular weight of sample, necessarily decreases the total surface area available for reaction. This decreased surface, as expected, resulted in decreasing the reaction rate constant in an amount inversely proportional to the square of the particle size ( $1/r^2$ ).

Since the rate constant in this nuclei growth model is a function of the square root of the diffusion constant<sup>5</sup> the variation of the rate constant with the absolute temperature can be used to construct an Arrhenius plot (Fig. 3). In this situation the slope of the Arrhenius plot will be  $E_a/2$  and the slope must be doubled to obtain the procedural activation energy. This value, calculated by least squares analysis is 108 kcal/mole.

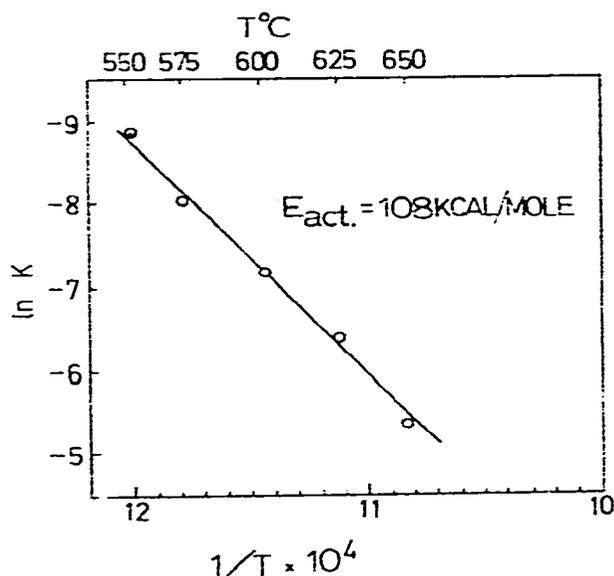


Fig. 3. Arrhenius plot for the  $\text{K}_2\text{CO}_3 + \text{PbO} \cdot \text{SiO}_2$  reaction.

To insure that the lead metasilicate grains were completely and continuously covered with potassium carbonate particles experiments were performed in which the stoichiometric amount of potassium carbonate was doubled and tripled. The increase in potassium carbonate showed no effect on the rate constant or the values of  $m$ . Thus reacting lead metasilicate and potassium carbonate in 2:1 mole ratios is justifiable and each lead silicate sphere can be considered isolated in a continuous matrix of potassium carbonate. To further verify the boundary conditions of the experiments an electron microprobe analysis was made to determine the distribution of the lead metasilicate grains in the potassium carbonate matrix. These data reaffirmed that the lead metasilicate grains were completely and continuously covered with particles of potassium carbonate.

### B. $4\text{PbO}\cdot\text{SiO}_2 + \text{K}_2\text{CO}_3$ reaction

The data for the marker study was consistent with that in part A, *i.e.*, the diffusion was one-way transfer of  $\text{K}_2\text{O}$  as ions or molecules. The isothermal experiments were run from 550–650°C in 25°C increments. X-ray analysis of reactants and products shows the reaction to be



with no other compounds seen over the temperature range studied. The data relating the fraction of the reaction completed as a function of time at a given temperature were used, as was the case in part A to determine the model (Fig. 4). This reaction was found to be nuclei growth controlled with a value of  $m = \frac{2}{3}$  (Fig. 5). This implies one dimensional diffusion controlled growth with a decreasing nucleation rate.

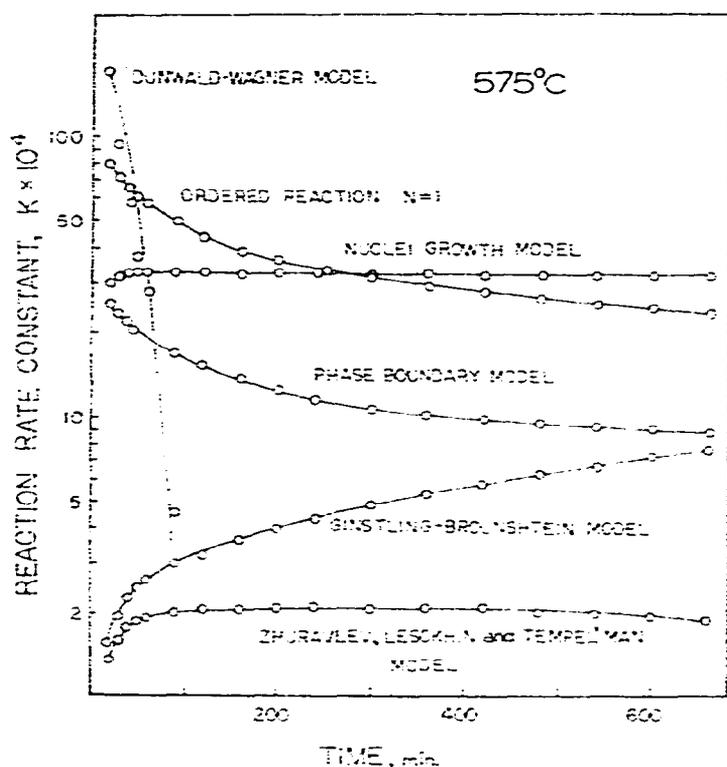


Fig. 4. Analysis of reaction rate equations for the  $\text{K}_2\text{CO}_3 + 4\text{PbO}\cdot\text{SiO}_2$  reaction.

As was the case in part A this nuclei growth model has a rate constant which is a function of the square root of the diffusion constant. A least squares analysis of the Arrhenius plot gave a procedural activation energy of 85 kcal/mole.

A potassium carbonate pellet held at 650°C for 48 hours showed no weight loss, and X-ray analysis of partially reacted sample showed no traces of  $\text{K}_2\text{O}$ , indicating the weight change due to the decomposition of the carbonate was indicative of a

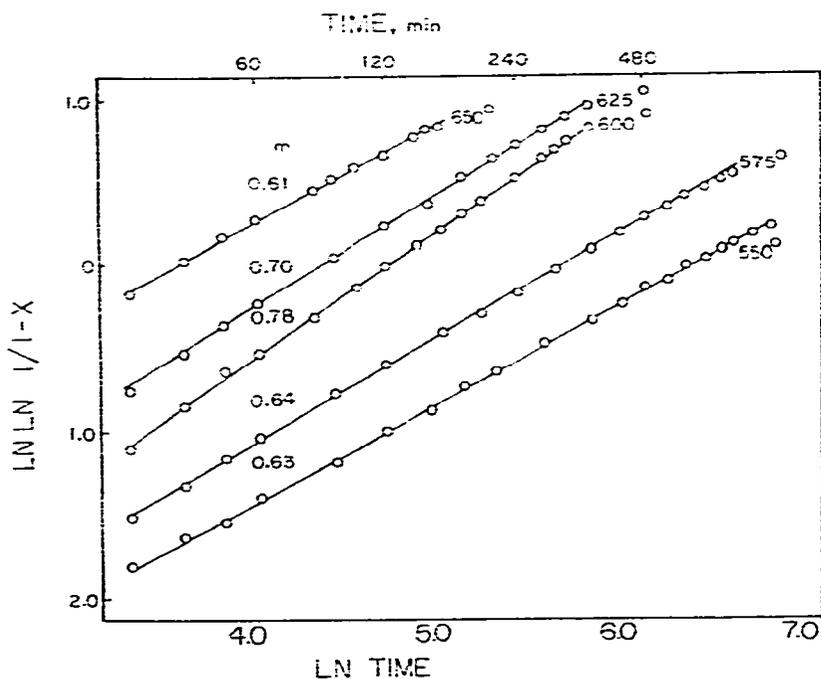


Fig. 5. Nuclei growth model for the  $K_2CO_3 + 4PbO \cdot SiO_2$  reaction.

reaction occurring and not the decomposition of  $K_2CO_3$  to  $K_2O$  in the presence of the lead silicate.  $PbO$  was present in the tetragonal form (litharge) at  $575^\circ C$  and below, and as orthorhombic massicot at  $600^\circ C$  and above. This polymorphic transformation created no observable effect on the reaction kinetics of the system.

Optical microscopy and electron microprobe analysis showed coarse lead silicate grains isolated in a continuous matrix of fine potassium carbonate particles.

The TG method of Sativa<sup>2</sup> is designed to determine the activation energy and the mechanism of a reaction from a single experiment. The advantages of evaluating reaction kinetics by a continuous increase in sample temperature are two fold. The amount of experimental data is reduced and the kinetics can be investigated over the entire temperature range of the reaction. Unfortunately, as Sativa has pointed out, the sensitivity of this method as with other TG methods is not great. From Fig. 6 it can be seen that all but one model gives approximately a straight line. This method does not provide much assistance in arriving at the proper mechanism, at least in this situation. The procedural activation energy is determined graphically and was found to be approximately 90 kcal/mole. This value is consistent with the value obtained in the isothermal experiments.

The method of Tets, Weidemann and Vaughan<sup>1</sup> has been previously demonstrated<sup>9</sup> to be an effective means of determining the procedural activation energy for solid-solid reactions. This method is, of course, fraught with the difficulty of any method of determining the procedural activation energy without a knowledge of the reaction mechanism. Gomes<sup>6</sup> has pointed out that with some mechanisms, *i.e.*,

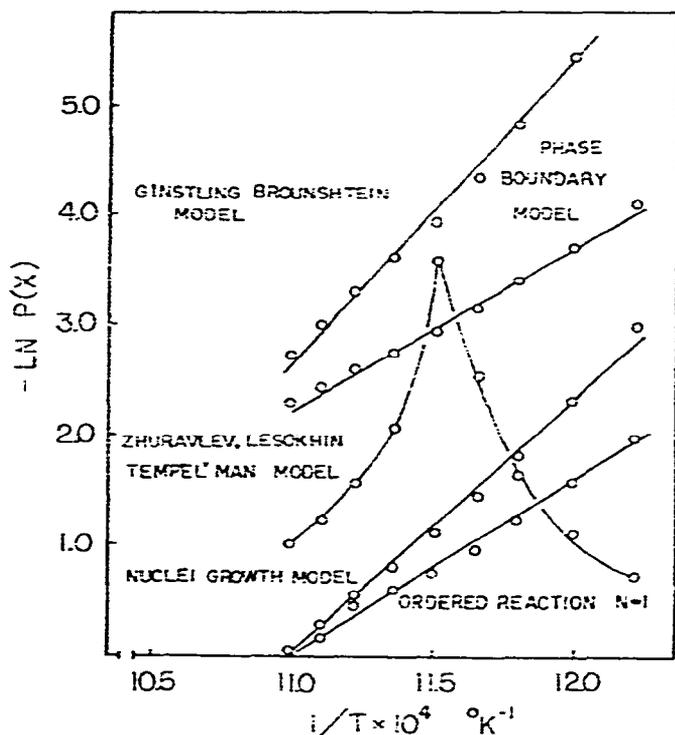


Fig. 6. TG method of Sativa for the  $K_2CO_3 + 4PbO \cdot SiO_2$  reaction.

phase boundary models, the activation energy has no significance and the units are not consistent with those for activation energies. In addition, until the nature of the relationship between the diffusion coefficient and the inverse of the absolute temperature is determined the exact value of the activation energy cannot be determined. In the experiments in this paper it was only through a knowledge of the mechanism that it was determined that the slope of the Arrhenius plot was  $E_a/2$  and not  $E_a$ .

Therefore, any method of determining the procedural activation energy without first determining the mechanism of the reaction may give very misleading results.

The method of Tets, Weidemann and Vaughan requires that the reaction rate at a certain established percent completion be plotted against the inverse of the absolute temperature at which this degree of completion is reached. This is generally

TABLE I  
ACTIVATION ENERGY AS A FUNCTION OF THE DEGREE OF COMPLETION OF REACTION FOR TG (METHOD OF TETS, WEIDEMANN AND VAUGHAN)

$x$	$E_a$
$\frac{1}{4}$	62
$\frac{1}{2}$	68
$\frac{3}{4}$	79

taken at  $x = \frac{1}{2}$ . In theory the results should be the same regardless of the degree of completion chosen. This aspect of the method was tested by taking the rate and temperature when the reaction was  $\frac{1}{8}$ ,  $\frac{1}{4}$  and  $\frac{1}{2}$  completed. The results are shown in Table 1.

As can be seen, the value of the activation energy at  $x = \frac{1}{2}$  is reasonably close to those determined isothermally. However, as data is taken at earlier stages in the reaction, the activation energy is seen to decrease substantially. The cause of this progressive error is not apparent, but it may create problems in the use of this method in solid-solid reaction kinetic work.

#### CONCLUSION

The solid-solid reaction between  $4\text{PbO} \cdot \text{SiO}_2$  and potassium carbonate to form  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$  and  $\text{PbO}$  is nuclei growth controlled and may be described by the equation:

$$-\ln(1-x) = K t^{0.66}$$

The value of 0.66 for the exponent infers one dimensional diffusion controlled growth with decreasing nucleation rate. The procedural activation energy was calculated to be 85 kcal/mole.

The solid-solid reaction between  $\text{PbO} \cdot \text{SiO}_2$  and potassium carbonate to form  $\text{K}_2\text{O} \cdot 2\text{PbO} \cdot 2\text{SiO}_2$  is also nuclei growth controlled and may be described by the equation:

$$-\ln(1-x) = K t^{0.5}$$

The value of 0.5 for the exponent infers a one dimensional diffusion controlled model with zero or decreasing nucleation rate. The procedural activation energy was found to be 108 kcal/mole.

The TG method of Tets, Weidemann and Vaughan<sup>1</sup> and Sativa<sup>2</sup> were utilized to study the reaction between  $4\text{PbO} \cdot \text{SiO}_2$  and  $\text{K}_2\text{CO}_3$ . Both methods yielded procedural activation energies consistent with those obtained by isothermal techniques. However, the method of Sativa was found not to be sufficiently sensitive to allow determination of the specific reaction mechanism.

#### ACKNOWLEDGEMENT

The authors would like to express their appreciation to J. Male, M. Wood, G. Ganzala, for reading the manuscript.

This work was part of the James Slade Scholar program. Without the assistance of Professors E. J. Smoke, W. H. Bauer and A. J. Deaning this program would not have been possible.

## REFERENCES

- 1 A. V. Tets, H. G. Weidemann and H. P. Vaughan, presented at the *Pittsburgh Conference on Analytical Chemistry and Applied Spectroscopy (1966)*.
- 2 V. Sativa, *Thermochim. Acta*, 2 (1971) 423.
- 3 W. Jander, *Z. Anorg. Chem.*, 1 (1927) 163.
- 4 A. M. Ginstling and B. I. Brounstein, *J. Appl. Chem. USSR*, 23 (1950) 1327.
- 5 S. F. Hulbert, *J. Brit. Ceram. Soc.*, 1 (1968) 11.
- 6 W. Gomes, *Nature*, 192 (1961) 855.
- 7 R. E. Carter, *J. Amer. Ceram. Soc.*, 43 (1961) 116.
- 8 R. F. Geller and E. N. Bunting, *J. Res. Nat. Bur. Stand.*, 17 (1936) 283.
- 9 W. R. Ott, in S. Bayer (ed.), *Proceedings Third International Conference on Thermal Analysis*, Birkhäuser, Verlag, Basel, in press.