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THERMAL AND KINETIC STUDIES OF STRONTIUM OXALATE CRYSTALS

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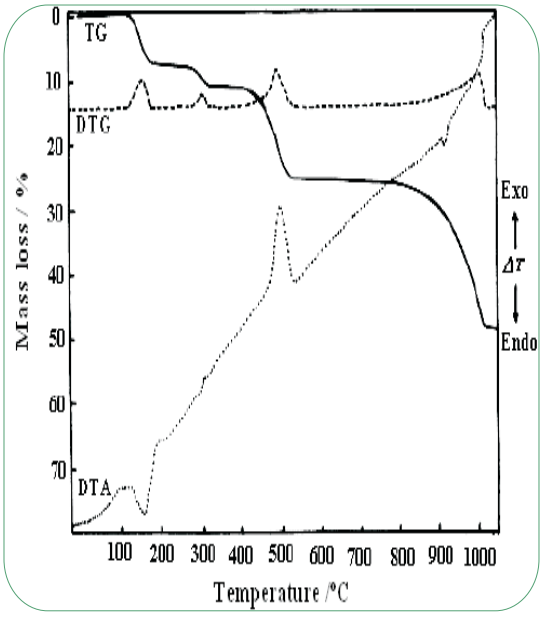
ABSTRACT

Single crystals of strontium oxalate have been grown using gel method at ambient temperature. Thermal characteristics and kinetic parameters of strontium oxalate crystals were determined by thermo-gravimetric analysis (TG) under non-isothermal heating conditions. The pyrolysis experiments were performed with increasing temperature up-to 600^{0}C at heating rate of 5, 7 and 10^{0}C in nitrogen gas atmosphere. The pyrolysis curve showed that loss of mass took place mainly in the range of 250-360^{0}C. At higher temperature there was a significant mass loss due to decomposition of oxalates. Ozawa and Coats & Redfern methods were used to determine the apparent activation energies of material degradation. The apparent activation energies for strontium oxalate crystal were obtained 220.42 and 230.53 KJ/mol for the respective methods.

KEYWORDS : *Strontium oxalate, Thermo-gravimetric analysis, Kinetic studies, thermodynamic parameters .*

INTRODUCTION

Pyro and kinetic studies such as reaction rate and activation energy are important parameters to determine the reaction mechanism in solid phases. Thermogravimetric analysis gives valuable information about practical applications of the material. The decomposition of strontium oxalate in strontium carbonate along with water molecules and carbon monoxide leads to produce yellow colour in fire crackers [1]. The stability of the strontium oxalate up-to 200^{0}C shows prominent use of this material to produce hardness with strontium titinate in capacitor industries [2]. Dollimore et.al [3] studied and reported thermogravimetric analysis of number of metal oxalates. In



the present work thermogravimetric analysis of grown material has been extensively used as a means of determining pyrolysis characteristics and also to determine the kinetics parameters. Non-isothermal thermo-gravimetric analysis has been applied in the study of the kinetics of thermal decomposition of grown crystals. It was shown that the decomposition process involves two consecutive first order reactions. Barium oxalate decomposes to barium carbonate and liberating water as well as carbon monoxide. At higher temperature it further decomposes to strontium oxide and release carbon dioxide. The integral method was used in the analysis of thermogravimetric data to determine pyrolysis kinetics. It was observed that total mass loss was mainly dependent on the final temperature and to lesser

extant on the heating rate employed. In the decomposition reaction, the main reason of mass loss corresponding to decomposition of oxalates into carbonates by releasing water molecules, carbon monoxide and a significant mass loss at higher temperature was attributed to carbonate decomposition.

EXPERIMENTAL

The thermogravimetric curves were obtained by employing a thermal analysis-TA-2050 thermal analyzer under various heating rates in nitrogen gas atmosphere as shown in Figure 1. About 10-14mg powder of gel grown strontium oxalate [4] material was used for each measurement. The integral residual weights were recorded between 30^{0}C to 600^{0}C. However, the kinetic data analysis was performed based on the results between 250^{0}C to 360^{0}C, where the rigorous reaction actually took place. Three heating rates 5^{0}C/min, 7^{0}C/min and 10^{0}C/min were used in this study. In recent years, there has been increasing great interest in determining the rate-dependent parameters of solid-state non-isothermal decomposition reactions by analyzing TG curves. A TG study consists of performing a kinetic analysis, which includes weight loss curves, obtained at different heating rates in order to deduce the dependence of the kinetic parameters with the conversion. The Ozawa [5] and Coats & Redfern [6] integral methods were used for kinetic data analysis.

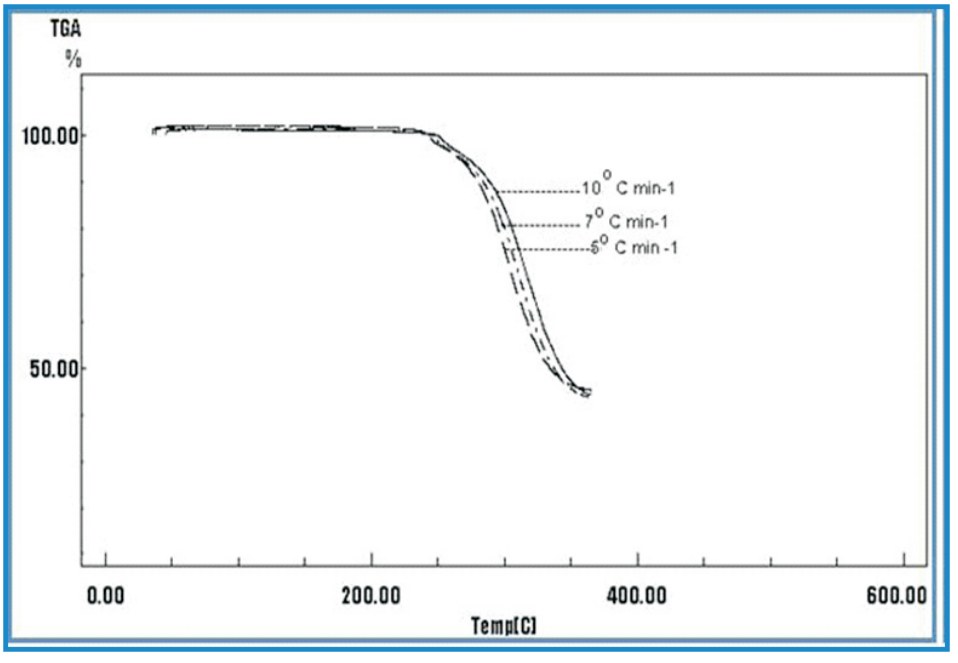


Figure 1: The thermogravimetric curves at three different rates

The Ozawa Method

$\log \beta = \log(AE/R) - 2.315 - 0.4567(E/RT) - \log g(a)$ .....(1)

where β is the heating rate (K min^{-1}), A is the pre-exponential factor(min^{-1}), R is the gas constant (8.314 Jmol^{-1}K^{-1}) and

$g(a) = (AE/\beta R)P(x)$ .....(2)

$x = E/RT$ .....(3)

a is the fraction reacted

$a = (W_0 - W_t)/(W_0 - W_f)$ .....(4)

where W0 is the initial mass of the sample, Wt is the mass of the sample at temperature t and Wf is the final mass at a temperature at which the mass loss is approximately unchanged.

In this method, heating rates with temperature are compared under the five different conversion rates. Graphs are plotted between natural logarithm of heating rate versus reciprocal of temperature for each value of conversion rate as shown in Figure 2. These graphs are of straight-line nature, which could be thus used to obtain activation energy (E) and frequency factor (A).

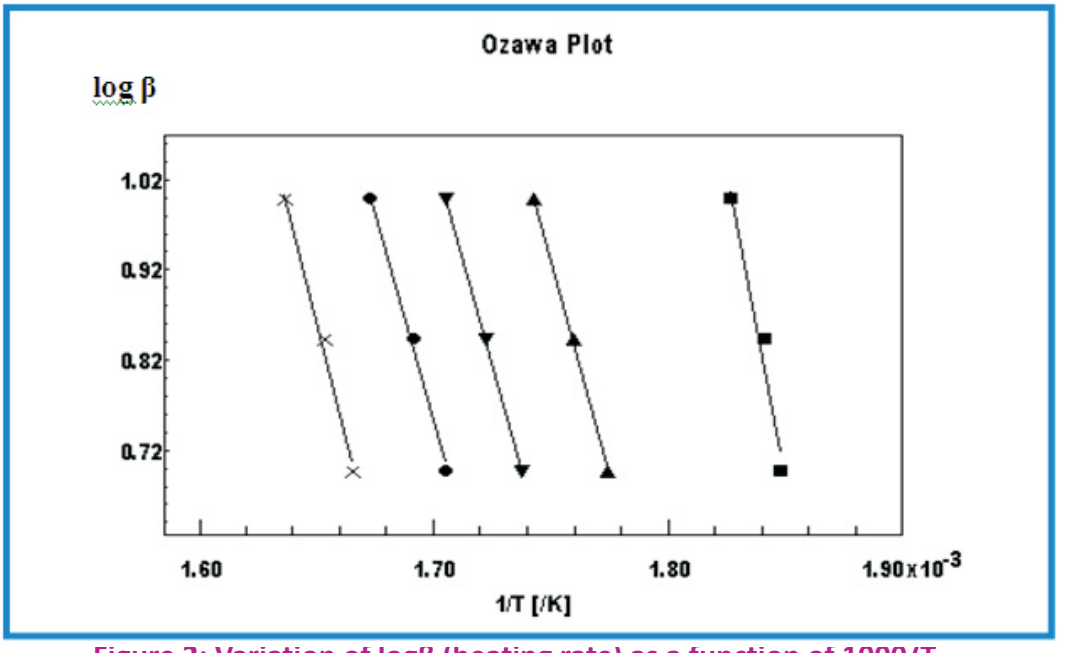


Figure 2: Variation of logβ (heating rate) as a function of 1000/T

The Coats & Redfern method

$$\log\left[\frac{1-(1-\alpha)^{1-n}}{T^2(1-n)}\right] = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\,RT} \qquad \text{for } n \neq 1 \quad \text{.....(5)}$$

$$\log\left[\frac{-\log(1-\alpha)}{T^2}\right] = \log\frac{AR}{\beta E}\left[1-\frac{2RT}{E}\right] - \frac{E}{2.303\,RT} \qquad \text{for } n = 1 \quad \text{.....(6)}$$

By plotting appropriate left-hand side of the above equations (5) and (6) versus 1/T into a straight lines as shown in figure 2, help in calculating E and A.

The other kinetic analysis parameters such as enthalpy of activation (ΔH*), entropy of activation (ΔS*) and free energy change of decomposition (ΔG*) were evaluated using equations [7-9]-

ΔH^* (KJ mol^{-1}) = E +ΔnRT .....(7)

where Δn = Number of moles of product − number of moles of reactant in the reaction

$\Delta S^* (JK^{-1}mol^{-1}) = 2.303\ R\ [\log (Ah/KT)]$ .....(8)

$\Delta G^* (KJ\ mol^{-1}) = \Delta H^* - T\Delta S^*$ .....(9)

where A is (Arrhenius constant) determined from the intercept, K is Boltzmann and h is Plank's constant.

RESULTS AND DISCUSSION

Figure 1 shows thermogravimetric (TGA) curves of a sample at the various heating rates. In Ozawa method, the graph shown in Figure 2 is plotted between log (heating rate) versus 1000/T for five different conversion rates ranging from 0.1 to 0.6. The slopes of these five straight lines have been used to calculate activation energy (E) and their intercepts were used to calculate frequency factor (log A). The other kinetic parameters such as enthalpy of activation (ΔH*), entropy of activation (ΔS*), and free energy change of decomposition (ΔG*) were calculated using equations (7),(8), and (9) and are represented in Table1. Figure 3 is the best linear fitted plot obtained using equation (6) for Coats & Redfern method. The average calculated activation energy. Frequency factor and other thermodynamic parameters were also calculated using equation (7), (8) and (9), and that are tabulated in Table 1.

The results obtained by the Ozawa method seem to be in good agreement with the results calculated by Coats-Redfern method. The positive value of ΔH* indicate that the dissociation processes are endothermic in nature and enhanced with the rise of temperature [9]. ΔG* values are positive, thus dissociation processes are non-spontaneous [10]. The positive values of ΔS* indicate that the activated complex has a less ordered structure than the reactants [10] and further the high values of A indicate the fast nature of the reaction [11]. The overall activation energy

Table 1: Kinetics and thermodynamic parameters of dehydration of strontium oxalate

Method	K (min^{-1})	E (KJ/mole)	? H^* (KJ/mole)	? S^* (KJ/moleK^o)	? G^* (KJ/mole)	Frequency factor (A)
Ozawa	$1.25X10^{10}$	220.42	216	63.8	185	$2.22X10^{16}$
Coats & Redfern	$1.8X10^{10}$	230.53	227	74.4	191	$9.3X10^{16}$

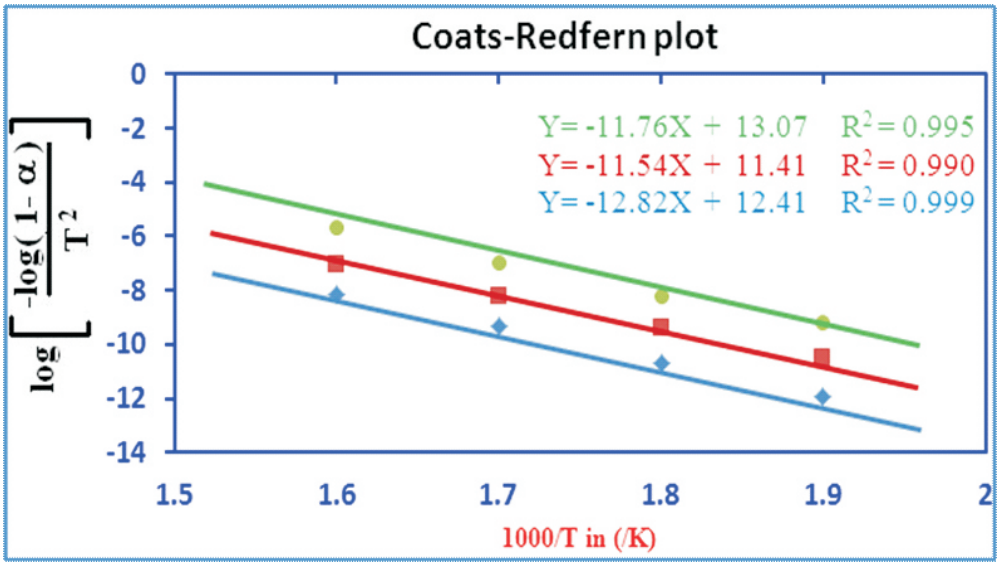


Figure 3: $\log\left[\frac{-\log(1-\alpha)}{T^2}\right]$ a as a function of 1000/T

for thermal decomposition 220.42 KJ/mole calculated by Ozawa and 230.53 KJ/mole calculated by Coats-Redfern methods are very close to each other. These values reveal that the compound is much more stable, and supported its application to improve hardness of titanate material in capacitor industries [2].

CONCLUSIONS

In summary, the kinetic data of analysis was performed between 2500C to 3600C. The overall activation energy and other thermodynamic parameters for thermal decomposition calculated by Ozawa and Coats-Redfern methods are very close to each other. The values of activation energy reveal that the compound is more stable and hence can be used to improve the hardness of ceramic material.

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