# Thermal Decomposition Kinetics of 2CsBr·LaBr₃·10H₂O

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A novel solid compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$ was found, separated and tested during studying the phase equilibria of the ternary system of $CsBr–LaBr_3–H_2O$ at 298.2 K and the thermal stability of the compound was studied by thermogravimetry and differential thermogravimetry. Three weight-loss phases were observed in the heating courses from room temperature to 400 °C in the inert atmosphere, in which 2, 5, 3 of water molecules were removed from the compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$ in turn. By Kissinger and Ozawa methods, the activation energies of thermal decomposition at three weight-loss phases were obtained as 58.5213, 210.2401 and 149.6305 kJ mol$^{-1}$, respectively. Meanwhile, reaction orders of three thermal decomposition reactions were found with the values of 0.3574, 0.4761, 0.3209, respectively. Thermal decomposition kinetic equation of $2CsBr \cdot LaBr_3 \cdot 10H_2O$ at three weight-loss processes could be expressed as the following forms: $d\alpha/dt = 42.3473 \cdot \exp(-58521.3/RT) \cdot (1-\alpha)[-\ln(1-\alpha)]^{-1.7979}$ for the 1st phase, $d\alpha/dt = 1.5689 \times 10^{25} \cdot \exp(-210240.1/RT) \cdot (1-\alpha)[-\ln(1-\alpha)]^{-1.1004}$ for the 2nd phase and $d\alpha/dt = 2.0189 \times 10^{12} \cdot \exp(-149630.6/RT) \cdot (1-\alpha)[-\ln(1-\alpha)]^{-2.1163}$ for the 3rd phase.

Keywords: Cesium bromide, Lanthanum bromide, Solid compound, Thermal decomposition kinetics, Thermal analysis.

## INTRODUCTION

Compounds containing lanthanide ions with versatility and specificity have wide application prospects in biology, medical diagnosis, sensing, photovoltaic cells, solar energy conversion, hydrogen fuel storage, trichromatic fluorescent lamps, and other fields[1-4]. More and more efforts had been devoted in the work of searching, finding and characterizing the basic thermodynamic properties of new compounds containing lanthanides. In the previous paper we reported the phase equilibria of the ternary system of $CsBr–LaBr_3–H_2O$ at 298.2 K, in which the solid phases of $2CsBr \cdot LaBr_3 \cdot 10H_2O$ was formed, and incongruently soluble in water[5]. The novel solid phase compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$ was characterized by chemical analysis, XRD and TG-DTG techniques. In order to master further the thermal stability of the solid phase compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$, in this paper the thermal stability properties were investigated. Thermal stability study is important to provide certain theoretical basis to the storage, stability value and period of validity prediction to the compound[6,7]. With this in view, this work was undertaken to study the thermal decomposition kinetics of the solid $2CsBr \cdot LaBr_3 \cdot 10H_2O$ by means of thermoanalysis technology. Firstly, weight-loss process of $2CsBr \cdot LaBr_3 \cdot 10H_2O$ was obtained by thermogravimetry (TG) and differential thermogravimetry (DTG). Secondly, pyrolysis kinetics parameters were calculated by thermal analysis theory. Lastly, the kinetic equation of thermal decomposition was derived[8].

## EXPERIMENTAL

The novel compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$ was prepared in the ternary system of $CsBr–LaBr_3–H_2O$ at 298.2 K in our laboratory. Meanwhile, it was verified. The simultaneous TG/DTA curves were obtained with Netzsch STA 449S3 thermoanalyzer (German NETZSCH Co.) in nitrogen atmosphere.

**Measurement of TG-DTG curves:** In the whole study, TG thermoanalyzer working temperature was controlled from room temperature to 400 °C. Heating rate was fixed at 5, 10, 15, 20 and 25 °C min$^{-1}$ in a dynamic nitrogen atmosphere with 30 mL min$^{-1}$ of flow. The sample of 8-10 mg was placed in an $Al_2O_3$ crucible sample cell of 100 μL volume.

## RESULTS AND DISCUSSION

**TG-DTG analysis of 2CsBr·LaBr₃·10H₂O:** TG, DTG curves of the thermal decomposition of the compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$ conducted at a heating rate of 5 °C min$^{-1}$ was shown in Fig. 1. From the Fig. 1, three loss-weight processes were observed and the first loss-weight yield was nearly 3.66 %, the second almost 8.95 % and the last approximately 5.81 %, indicating in the first loss-weight process two water molecules were lost, and in the second process five water molecules lost
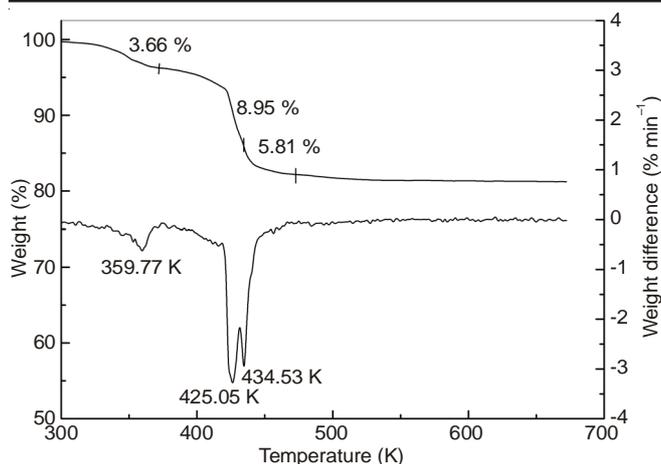
Fig. 1. TG-DTG curves of $2CsBr \cdot LaBr_3 \cdot 10H_2O$

and in the last three water molecules lost at the decomposition temperatures. The total weight loss is 18.42 % and equal to the ratio of $H_2O$ in the compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$ compared with the calculated value of 18.31 %. Meanwhile, according to the TG analyzing effects, the thermal decomposition temperature of every loss-weight phase increased with the rising of heating rate at 5, 10, 15, 20 and 25 °C min$^{-1}$ and the peak-temperature values of first phase were 86.77, 97.13, 103.09, 108.06 and 116.96 °C, the second peak temperatures 152.05, 155.90, 159.43, 161.47 and 163.13 °C, the last peak temperatures 161.53, 166.02, 167.67, 175.85 and 179.71 °C at the heating rate of 5, 10, 15, 20 and 25 °C min$^{-1}$, respectively.

**Thermal decomposition kinetics study**

**Calculation of activation energy:** Activation energy ($E_a$) of solid-state reactions are usually determined by the Kissinger method and the Ozawa's method in literatures based on TG curves at the multiple heating rates without knowing the reaction kinetic function[9,10]. Therefore, in this study, Kissinger and Ozawa methods were applied to find the values of thermal decomposition $E_a$ for the compound $2CsBr \cdot LaBr_3 \cdot 10H_2O$.

The Kissinger method[11] is expressed in the natural logarithm form (eqn. 1):

$$\ln\left(\frac{\beta}{T_p^2}\right) = \ln\left(\frac{AR}{E_a}\right) + \ln\left(-\frac{df(\alpha)}{d\alpha}\right)_{ap} - \frac{E_a}{RT_p} \quad (1)$$

where $T_p$ is the peak temperature in the DTG curve, A the preexponential factor, R the gas constant, E the apparent activation energy and $\beta$ is the heating rate which is indicated as $\beta = dT/dt$. In terms of the Kissinger method if $\ln(\beta/T_p^2)$ is plotted *versus* $1/T_p$, $E_a$ can be easily derived from the slope of the curve plotted.

The Ozawa's method (eqn. 2)[12] which represents one of the integral methods can also determine $E_a$, and the Kissinger equation (eqn. 2) is following:

$$\log\beta + \frac{0.4567E_a}{RT} = C \quad (2)$$

From the eqn. 2, $E_a$ can be obtained from the slop of linear fitting of $\log(\beta)$ against $(1/T_p)$.

The plots of $\ln(\beta/T_p^2)$ *versus* $(1/T_p)$ based on Kissinger's method and $\log(\beta)$ *versus* $(1/T_p)$ by Ozawa's method were presented in Fig. 2. Fitting and calculating results were given in Table-1, where r was linear correlation coefficient and SD was standard square deviation.

Fig. 2 and Table-1 showed that linear correlations of $\ln(\beta/T_p^2)$ *versus* $(1/T_p)$ and $\log(\beta)$ *versus* $(1/T_p)$ by the two methods are apparent and the linear correlation coefficients of both are higher. These calculating results also illustrated that the two methods agreed very well with each other in estimating the activation energy of the thermal decomposition of $2CsBr \cdot LaBr_3 \cdot 10H_2O$. The mean values of $E_a$ at three weight-loss processes were 59.6527, 210.2401 and 149.6305 kJ mol$^{-1}$, respectively.

**Calculation of pre-exponential factor and reaction order:** To establish the most probable kinetic functions for the decomposition of $2CsBr \cdot LaBr_3 \cdot 10H_2O$, the data of $\alpha$(conversation ratio), $d\alpha/dT$ (the rate of conversation) and T(absolute temperature) were obtained from TG/DTG curve at the heating rate of 5 °C min$^{-1}$. The thermal decomposition kinetic equation under non-isothermal conditions could be expressed as follows[13]:
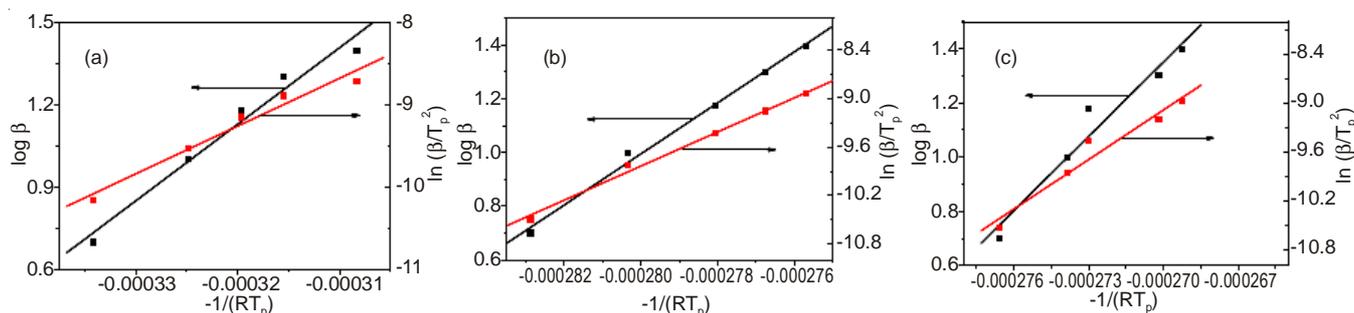


Fig. 2. Relation curve of finding activation energy from Kissinger and ozawa method; (a) the 1st phase (b) the 2nd phase (c) the 3rd phase

| | TABLE-1 | | | | | | | | |
| --- | --- | --- | --- | --- | --- | --- | --- | --- | --- |
| | ACTIVATION ENERGY AT EVERY PHASE BY KISSINGER'S AND OZAWA'S METHOD | | | | | | | | |
| Method | 1st Phase | | | 2nd Phase | | | 3rd Phase | | |
| | $E_a$ (kJ mol$^{-1}$) | r | SD | $E_a$ (kJ mol$^{-1}$) | r | SD | $E_a$ (kJ mol$^{-1}$) | r | SD |
| Kissinger | 58.1185 | 0.9834 | 0.1207 | 212.0367 | 0.9966 | 0.0589 | 149.4569 | 0.9703 | 0.0992 |
| Ozawa | 61.1869 | 0.9866 | 0.0521 | 208.4434 | 0.9968 | 0.0255 | 149.8042 | 0.9856 | 0.2287 |
| Mean | 59.6527 | | | 210.2401 | | | 149.6305 | | |
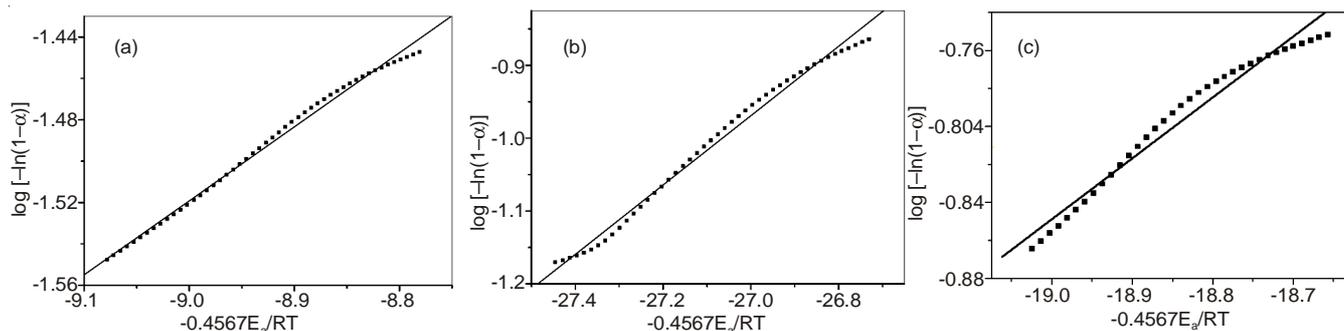
Fig. 3. Relation curve of log [-ln(1-α)] *vs.* 1/T_p at the different phase; (a) the 1st phase (b) the 2nd phase (c) the 3rd phase

$$d\alpha / dt = A\exp(-E_a / RT)f(\alpha) \qquad (3)$$

$$G(\alpha) = A\exp(-E_a / RT)\cdot t \qquad (4)$$

where f(α), G(α) are the differential and integral kinetics functions, respectively. Their relationship could be expressed as:

$$f(\alpha) = \frac{1}{d[G(\alpha)]/ d\alpha} \qquad (5)$$

In the study, Satava-Sestak integral equation in the following form[14,15] is applied:

$$\log[G(\alpha)] = \log\left(\frac{AE_a}{\beta R}\right) - 2.315 - 0.4567\frac{E_a}{RT} \qquad (6)$$

After trying out, the function form f(α) = n(1-α)[-ln (1-α)]^{1-1/n} and G(α) = [-ln(1-α)]^{1/n} were applied to find kinetics equation parameters. On basis of the decomposition differential and integral kinetics equations, the values of A and n were calculated by Satava-Sestak integral method. By plotting log [-ln(1-α)] against 1/T to fit linear, n and A were obtained from the slope and intercept of the plot, respectively. The thermal decomposition kinetics parameters were found using TG data at the heating rate of 5 °C min⁻¹. The fitting curve was shown in Fig. 3. The reaction orders (n) of three loss-weight processes were 0.3574, 0.4761, 0.3209, respectively. The following thermal decomposition kinetics equation of 2CsBr·LaBr₃·10H₂O were obtained:

The first phase: dα/dt = 42.3473·exp(−58521.3/RT)· (1−α)[−ln(1−α)]^{−1.7979}; The second phase: dα/dt = 1.5689 × 10²⁵·exp(−210240.1/ RT)·(1−α)[−ln(1−α)]^{−1.1004}; The last phase: dα/dt = 2.0189 × 10¹²·exp(−149630.6/ RT)·(1−α) [−ln(1−α)]^{−2.1163}.

## Conclusion

The thermal decomposition process on 2CsBr·LaBr₃·10H₂O was studied by thermoanalysis technique and thermodynamic treatment. The compound 2CsBr·LaBr₃·10H₂O had three loss-weight phenomena in the course of heating in inert atmosphere, and the loss-weight were all hehydrating process. Furthermore, the thermal decomposition kinetics equation at three phases were derived by TG and DTG data. The study is of great significance in predicting property and thermal stability of the compound 2CsBr·LaBr₃·10H₂O.

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