THERMAL DECOMPOSITION OF ZINC CARBONATE HYDROXIDE HYDRATE POWDERS OF DIFFERENT PARTICLE SIZE AND SAMPLE MASS①

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ABSTRACT The zinc carbonate hydroxide hydrate ($Zn_4CO_3(OH)_6 \cdot H_2O$) was prepared by using chemical precipitate method and its crystal form was identified by XRD. Effects of sample particle size and mass on the thermal decomposition in the process of preparing ZnO powder were investigated by DTA. The results showed that the zinc carbonate hydroxide hydrate is decomposed in the temperature range from 430~ 570K, only one endothermic peak in the DTA curve has been observed, the particle size and the sample mass of zinc carbonate hydroxide hydrate have no effects on the decomposition process. In this decomposition reaction, the kinetic parameters for the decomposition process were calculated as $n = 0.8$, $E = 113$ kJ/mol, $A = 1.3 \times 10^{12} s^{-1}$, respectively.

Key words zinc carbonate hydroxide hydrate thermal decomposition ZnO powder

1 INTRODUCTION

ZnO varistors are the ceramic devices that have excellent non-linear current-voltage (I-V) characteristics and energy absorption ability, which make them valuable as voltage suppressers in power systems and electronic circuits[1,2]. In these varistors, the ZnO content is more than 80% ~ 90%. The methods of preparing ZnO powders are adding the precipitating agent into aqueous solution of zinc salts, then the ZnO powders are obtained by thermal decomposition. The two-step reaction scheme is illustrated in the following equation:

$$Zn^{2+}(aq) + \text{precipitating agent} \longrightarrow Zn_n(XY)_m \downarrow \xrightarrow{\text{Heating}} ZnO$$

In this reaction, the most normal zinc salts are $ZnSO_4$ and $ZnCl_2$. The normal precipitating agents include $NH_3 \cdot H_2O$, Na_2CO_3 and $(NH_4)_2C_2O_4$. In preceding work, we investigated the microstructures of three different ZnO powders prepared by chemical precipitation method using $ZnSO_4 \cdot 7H_2O$ as original material, using Na_2CO_3, $(NH_4)_2C_2O_4$ and $NH_3 \cdot H_2O$ as precipitating agents. It has been found that using Na_2CO_3 as precipitating agent the decomposition temperature is lowered and product is suitable to make the ZnO-based varistor[3,4]. It is very clear that the thermal decomposition is an essential process for the ZnO preparation. It is well known that the kinetics of thermal decomposition of solids depends largely on the sample and reaction conditions. This is due to the complexity of the kinetic process[5]. The particle size[6] and the sample mass[7] are two factors that affect the process of decomposition. There-

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fore, it is necessary to determine the process of the decomposition using DTA technique. In this paper, the effect of particle size and the sample mass on the decomposition of zinc carbonate hydroxide hydrate were studied in detail.

2 CALCULATION OF KINETIC PARAMETERS

There are many different methods in calculating the thermal kinetic parameters from a DTA (or TG) curve. Doyle-Ozawa's method, Kissinger's method, Freeman-carroll's method and Anderson-Freeman's method are used frequently. In general, the expression of solid decomposition reaction of nth order can be described as

$$\frac{dx}{dt} = A(1-x)^n e^{-E/RT} \quad (1)$$

where x is the fraction of material reacted, t is time, n reaction order, E activation energy, R gas constant, T absolute temperature.

From eqn. (1), according to literature[8], the following equation can be obtained:

$$n = 0.99811 - 1.25873e^{-0.93573(T_e-T_m)/(T_m-T_{il})} \quad (2)$$

$$E = \frac{RT_0^2}{T_m - T_e}\ln(1-n) \quad (3)$$

$$A = \frac{(E\varphi/RT_0^2)e^{E/RT_0}}{e^{[E(T_m-T_0)]/RT_0^2} + (n-1)} \quad (4)$$

where T_{il} is the inflection temperature, T_m is peak temperature of DTA curve, T_0 and T_e the starting and final decomposition temperature of DTA curve. Eqn. (2) is only used in the range of $n < 1$. The reaction order of decomposition can be calculated by using this equation. After obtaining the value of n, the values of E and A can be calculated by using Eqns. (3) and (4). When n is in the range of $n \neq 1$, the following equation is valid.

$$n = 352204.38e^{-18.126(\Delta T_{il}/\Delta T_m)} \quad (5)$$

$$E = RT_0^2/(T_m - T_{il})\ln[[2 + n + \sqrt{n(n+4)}]/2] \quad (6)$$

The values of the pre-exponential factor A in this category still can be calculated by using Eqn. (4). When n is equal to 1, the following equation can be obtained:

$$A = \frac{\varphi E}{RT_m^2}e^{E/RT_m} \quad (7)$$

$$E = T_{il}[26.92236 + 7.1305 \times 10^{-19}e^{47.05882(T_{il}/T_m)}] \quad (8)$$

where φ is the constant heating rate.

In addition, Kissinger[9] pointed out that the reaction order n can be obtained from the shape index (I). Fig. 1 is a traditional endothermic peak.

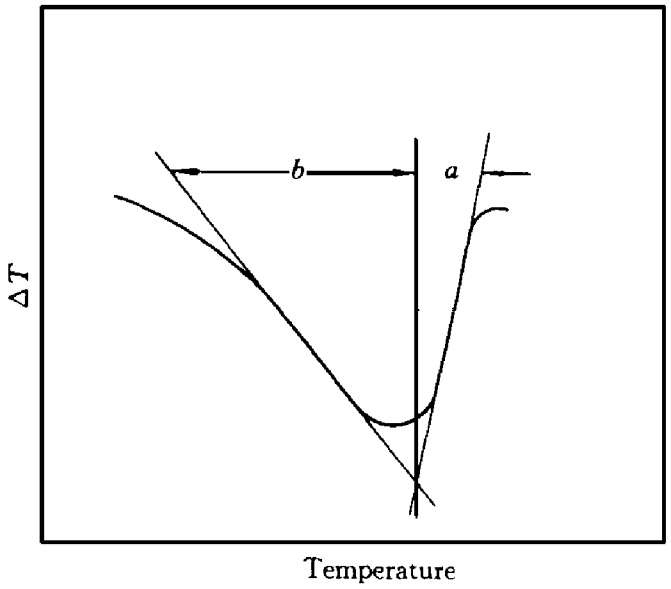

Fig. 1 Shape index for peak of DTA curve

The shape index (I) can be described as following:

$$I = a/b \quad (9)$$

The relation of n to I is

$$n = 1.26I^{1/2} \text{ or } I = 0.63n^2 \quad (10)$$

Here Eqn. (10) is a semi-empirical equation. In this paper, all of the reaction orders n were estimated by Kissinger's method at first, then the kinetic parameters n, E, and A were evaluated accurately from Eqn. (2) to Eqn. (8).

3 EXPERIMENTAL PROCEDURE

3.1 Sample preparation and characterization

The sample was prepared by adding 5.0% Na_2CO_3 (reagent grade) aqueous solution as precipitating agent into 0.1 mol/L $ZnSO_4$ aqueous solution, at the same time the solution was stirred with a machine at room temperature. The white precipitate was filtered then washed using distilled water and dried at 110 ℃. This precipitate is easy to agglomerate and shape large

grains. Therefore, in the process of dehydration the samples of different particle sizes were produced by grinding the large grains in a normal mortar. The particle size of the sample was 0.3 ~ 0.125 mm, 0.125 ~ 0.097 mm, 0.097 ~ 0.088 mm and < 0.088 mm. The phase of the precipitated powder was determined by XRD. The microstructure of zinc carbonate hydroxide hydrate powders was observed with a XPA-I model microscope.

3.2 Thermal decomposition experiment

The thermal decomposition was determined by using Rigaku Thermflex DTA equipment at some different heating rate in flowing nitrogen at a rate of 200 mL/min. Platinum sample cells and α-Al_2O_3 reference material were used for the DTA measurements.

4 RESULTS AND DISCUSSION

The X-diffraction pattern is illustrated in Fig. 2.

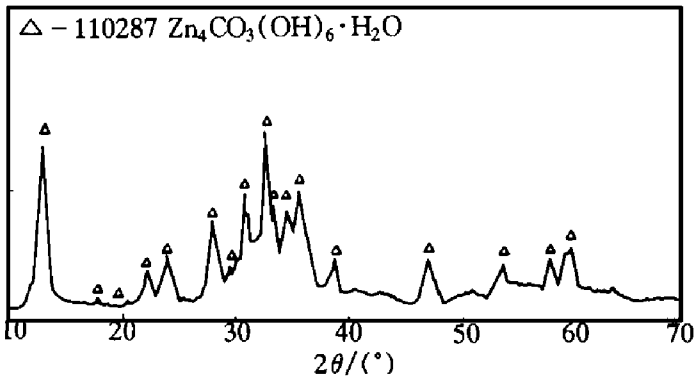

Fig. 2 XRD patterns for precipitate

The phase of the precipitate can be determined from Fig. 2. The molecular formula of the precipitate is $Zn_4CO_3(OH)_6 \cdot H_2O$. Fig. 2 shows that the diffraction peaks are more wider, this result shows amorphous tendency of the Zinc carbonate hydroxide hydrate. The precipitating reaction is represented by the equation:

$$Zn^{2+} + CO_3^{2-} + H_2O \longrightarrow Zn_4CO_3(OH)_6 \cdot H_2O \downarrow$$

Fig. 3 shows the DTA curves with different heating rate. Fig. 4 shows the XRD pattern of the sample at 573.2 K. The heating rate is an important factor to affect the decomposition process. The resolution can be increased when the heating rate is decreased. In general, there should be different peaks on the DTA curves, but it can be seen from Fig. 3 that there is only one endothermal peak on the DTA curves. The different heating rates just affect the peak temperature and the peak shape of DTA curves, the faster the heating rate, the higher the peak temperature and the sharper the DTA curves. Therefore, it can be concluded that the decomposition of the precipitate is carried out in only one step. The decomposition reaction of the sample can be represented by the following equation:

$$Zn_4CO_3(OH)_6 \cdot H_2O \longrightarrow ZnO_{(s)} + CO_{2(g)} \uparrow + H_2O_{(g)} \uparrow$$

The samples of different particle size are found to decompose at a heating rate of 10 ℃/min in a single step yielding a DTA curve similar to that shows in Fig. 3. and the ranges of peak temperature are about in 430 ~ 570 K.

The DTA curves of different sample mass are showed in Fig. 5. The results of kinetic parameters are listed in Table 1 and Table 2.

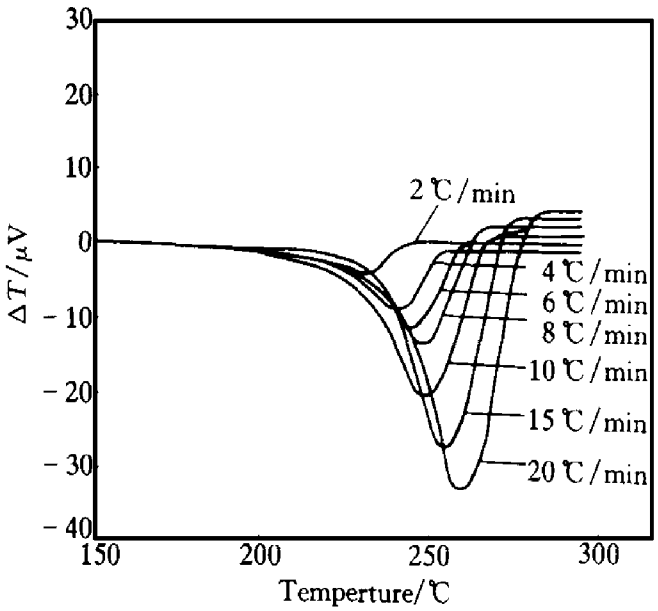

Fig. 3 DTA curves with different heating rate

There are many factors affect the results of the kinetic parameters. The particle size and the sample mass are two factors which affect the process of decomposition. For example, the par-

ticle size and the sample mass all can affect the thermal conductivity and gas diffusion so as to affect the rusults. But, Tables 3 and 4 show that the effects of the particle size and the sample mass on E, n and A are not obvious. Where n_K is the value calculated by Kissinger's method, n_L is the value calculated by the method of literature[8]. E is about equal to 113 kJ/mol, n to 0.8, A to $1.3 \times 10^{12} s^{-1}$ respectively. Fig. 6 is the micrograph.

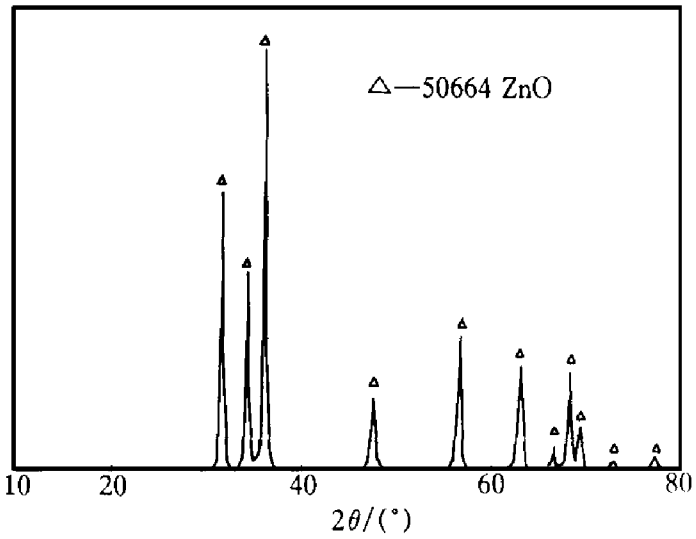

Fig. 4 XRD pattern of precipitate calcined at 573.2 K

The hole ratio is bigger between the particles in the loose sample and the ventilation property is very fine. The product gas (CO_2, H_2O) of thermal decomposition overflow easily from the sample surface into the carrying gas (N_2) so that the partial pressure of the product gas decreases speedily. The change of sample mass basically does not affect the ventilation when the sample quantities are small (< 20mg). The large particle size has made the heat conductivity and gas diffusivity in the solid very good, and the particle size almost does not affect above properties when the sample size changes little.

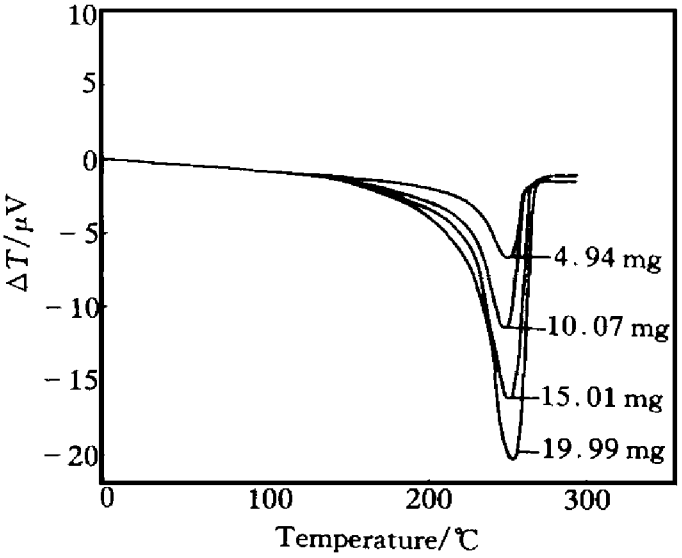

Fig. 5 Effects of differential mass on the DTA curve
(Particle size: 0.097~0.125 mm, heating rate: 10 ℃/min)

Table 1 The characteristic temperature of DTA curves with different particle sizes

Size/mm	T_0/K	T_{il}/K	T_m/K	T_e/K
0.3~0.125	430.0	515.0	525.0	547.0
0.125~0.097	431.2	515.0	526.2	548.0
0.097~0.088	441.2	515.6	526.2	549.2
< 0.088	434.4	516.2	526.2	548.4

Table 2 The characteristic temperature of DTA curves with different mass

Mass/mg	T_0/K	T_{il}/K	T_m/K	T_e/K
5.07	433.0	517.2	528.2	544.8
10.00	441.2	515.6	526.2	549.2
15.01	437.2	515.2	527.2	561.2
19.99	432.2	514.4	526.2	553.6

Table 3 Kinetic parameters of DTA curves with different particle sizes and mass of 0.2 mg

Size/mm	n_K	n_L	E/kJ·mol^{-1}	A/s^{-1}
0.3~0.125	0.89	0.87	112.46	9.1164×10^{11}
0.125~0.097	0.82	0.79	114.13	1.2597×10^{12}
0.097~0.088	0.77	0.83	113.25	1.3258×10^{12}
< 0.088	0.87	0.84	113.74	1.2517×10^{12}

Table 4 Kinetic parameters from DTA curves with different mass and particle sizes of 0.097~ 0.125 mm particle size

Mass/mg	n_K	n_L	E/kJ·mol^{-1}	A/s^{-1}
5.07	0.89	0.69	113.056	8.9739×10^{11}
10.00	0.77	0.83	113.25	1.3258×10^{12}
15.01	0.80	0.80	106.57	2.4579×10^{11}
19.99	0.79	0.85	122.761	9.1241×10^{12}

Fig. 6 The micrographes of Zinc carbonate hydroxide hydrate powder
(a) —× 80; (b) —× 500

In addition, there are also many various methods to calculate the kinetic parameters from the DTA (or TG) curve. The different methods will obtain the different results. Tables 3 and 4 still show that the n values estimated by using Kissinger's method are approximately equal to the values calculated by literature[8].

5 CONCLUSIONS

(1) The decomposition process is a single step, the DTA endothermic peak is only one. The decomposition temperature ranges is between 430 K and 570 K.

(2) The particle size and the sample mass do not affect the decomposition action. In this reaction, $n\approx0.8$, $E\approx113$ kJ/mol, $A\approx1.3\times10^{12}$s^{-1} respectively.

(3) The n values estimated by Kissinger's method are close to the values calculated by literature [8], which means that this calculation method is reliable.

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