Bull. Mater. Sci., Vol. 12, No. 5, December 1989, pp. 465–468. © Printed in India.

Thermal properties of barium–cadmium oxalate crystals

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MS received 26 September 1988; revised 29 May 1989

Abstract. The kinetics and thermodynamics of the thermal dehydration of crystalline powders of $BaC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ and $Ba_{1-x}Cd_xC_2O_4 \cdot 2{\cdot}5H_2O$ have been studied by means of thermogravimetry, as a function of temperature. The dynamic dehydration kinetics are also examined using DTA, recorded simultaneously with TG as a function of temperature. The validity of the estimated mechanism and kinetic parameters is briefly discussed. From DTA study it is concluded that all dehydration peaks are endothermic and the decomposition peaks of barium oxalate to barium carbonate, cadmium oxalate to cadmium oxide and barium cadmium oxalate to barium carbonate and cadmium oxide are exothermic.

Keywords. Kinetics; thermodynamics; barium oxalate; barium–cadmium oxalate crystals; thermal property.

1. Introduction

TGA and DTA studies on various oxalates have been described in general by Dollimore *et al* (1963) and it is reported that barium oxalate and cadmium oxalate decompose in nitrogen producing barium and cadmium metals, respectively, as the final products in a single reaction. The present paper deals with an investigation on the presence of different hydrates, the mechanism of dehydration and the kinetics and thermodynamics of the thermal dehydration of hydrated BaC_2O_4, CdC_2O_4 and $Ba_{0{\cdot}5}Cd_{0{\cdot}5}C_2O_4$ crystals by means of TGA and DTA.

2. Experimental

Thermogravimetric and differential thermal analysis of gel-grown hydrated barium oxalate (Dharmaprakash and Mohan Rao 1985), cadmium oxalate (Tomy and Arora 1981) and barium–cadmium oxalate (Dharmaprakash and Mohan Rao 1986) crystalline powders were carried out simultaneously using a DT-30 Shimadzu (Japan) automatic recording apparatus at a heating rate of 10°C min^{-1}.

3. Results and discussion

3.1 *Thermogravimetric and differential thermal analysis*

Gel-grown barium oxalate, cadmium oxalate and barium cadmium oxalate crystals at room temperature have the composition $BaC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ and $Ba_{0{\cdot}5}Cd_{0{\cdot}5}$, $C_2O_4 \cdot 2{\cdot}5H_2O$ respectively. Figure 1 shows the TGA plots of these crystals.

Taking the initial weight as standard, the course of decomposition is analysed by comparing their molecular weights. It is observed that the barium oxalate crystal

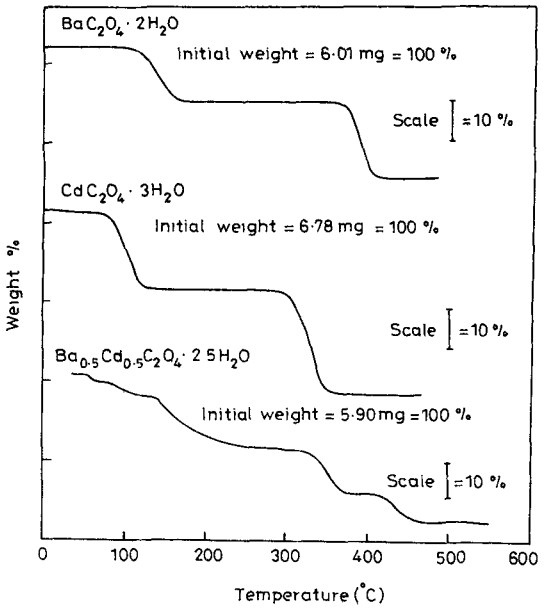

Figure 1. TGA plot of weight % vs temperature.

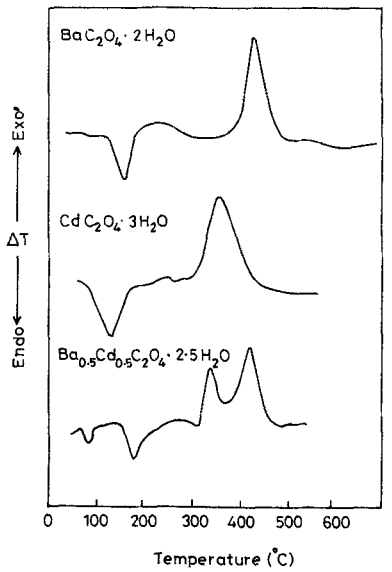

Figure 2. DTA curves for $BaC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ and $Ba_{0·5}Cd_{0·5}C_2O_4 \cdot 2·5H_2O$ crystals.

contains two molecules of water of crystallization, cadmium oxalate contains three molecules of water and barium cadmium oxalate contains 2·5 water molecules in the unit cell. Since the decomposition is carried out in air, the end product will certainly not reach the stage of metallic barium or cadmium, unlike the observations of Dollimore and Griffiths (1970) made in a nitrogen environment and at high

temperature. The weight loss in TGA experiments (figure 1) suggests that all the molecules of water associated with BaC_2O_4 are lost in one step. But in the case of $Ba_{0\cdot5}Cd_{0\cdot5}C_2O_4\cdot2\cdot5H_2O$, the water molecules are lost in two different steps.

The DTA technique involves the use of very small quantities of material. Since the comparison of DTA results from different sources is to some extent dependent on the type of apparatus and the method of operation, the analysis of $BaC_2O_4\cdot2H_2O$, $CdC_2O_4\cdot3H_2O$ and $Ba_{0\cdot5}Cd_{0\cdot5}C_2O_4\cdot2\cdot5H_2O$ has been undertaken using a standard procedure so that the thermal stability and pattern of decomposition of these crystals can be studied.

Figure 2 shows the DTA curves of $BaC_2O_4\cdot2H_2O$, $CdC_2O_4\cdot3H_2O$ and $Ba_{0\cdot5}Cd_{0\cdot5}C_2O_4\cdot2\cdot5H_2O$ respectively. The results (table 1) may be conveniently divided according to their decomposition. The general conclusion drawn from the observed results is that all dehydration peaks are endothermic and the decomposition peaks of oxalates into carbonates and oxides are exothermic.

In table 1, the first temperature shown is the point of departure from the base line and the second temperature is the temperature at which the maximum peak occurs.

On the basis of TGA and DTA studies, the following tentative mechanisms have been proposed for the thermal conversion of barium oxalate, cadmium oxalate and barium–cadmium oxalate.

$$BaC_2O_4\cdot2H_2O \xrightarrow{114°–148°C} BaC_2O_4 + 2H_2O,$$

$$BaC_2O_4 \xrightarrow{370°–415°C} BaCO_3 + CO, \quad (1)$$

$$CdC_2O_4\cdot3H_2O \xrightarrow{72°–122°C} CdC_2O_4 + 3H_2O,$$

$$CdC_2O_4 \xrightarrow{310°–355°C} CdO + CO + CO_2, \quad (2)$$

$$Ba_{0\cdot5}Cd_{0\cdot5}C_2O_42\cdot5H_2O \xrightarrow{50°–178°C} Ba_{0\cdot5}Cd_{0\cdot5}C_2O_4 + 2\cdot5H_2O,$$

$$2Ba_{0\cdot5}Cd_{0\cdot5}C_2O_4 \xrightarrow{370°–415°C} BaCO_3 + CdO + 2CO + CO_2. \quad (3)$$

3.2 *Kinetics and thermodynamics of thermal dehydration*

Many methods have been proposed for the kinetic analysis of solid state reactions by thermogravimetry (Brown *et al* 1980). The Coats and Redfern (1964) method is

Table 1. Summary of phase changes using DTA curves.

Crystal	Temperature (°C)	Decomposition
$BaC_2O_4\cdot2H_2O$	114°–148°	Endo dehydration
	370°–415°	Exo decomposition to barium carbonate
$CdC_2O_4\cdot3H_2O$	72°–122°	Endo dehydration
	310°–355°	Exo decomposition to cadmium oxide
$Ba_{0\cdot5}Cd_{0\cdot5}C_2O_4\cdot2\cdot5H_2O$	50°–75°	
	110°–125°	Endo dehydration
	140°–178°	
	310°–355°	Exo decomposition to cadmium oxide
	370°–415°	Exo decomposition to barium carbonate

Table 2. The extrapolated onset temperature T_{eo} from the DTA trace, the temperature of half dehydration $T_{\frac{1}{2}}$ from the TG trace, and the peak temperature T_P from the DTA trace for the dehydration of $BaC_2O_4 \cdot 2H_2O$, $CdC_2O_4 \cdot 3H_2O$ and $Ba_{0.5}Cd_{0.5}C_2O_4 \cdot 2.5H_2O$.

Dehydration temperature	Heating rate 10°C/min		
	$BaC_2O_4 \cdot 2H_2O$	$CdC_2O_4 \cdot 3H_2O$	$Ba_{0.5}Cd_{0.5}C_2O_4 \cdot 2.5H_2O$
T_{eo}	114	72	50
$T_{\frac{1}{2}}$	137	102	98
T_P	148	122	178

one of the methods of evaluating the kinetic parameters by means of dynamic TG (Zsako 1973). The general equation for obtaining the parameters is,

$$\ln (F(L)/T^2) = \ln AR/aE\,[1-(2RT/E)] - E(E/RT),$$

where $F(L)$ is a function depending on the mechanism of the non-isothermal dehydration, T the absolute temperature, R the gas constant and the linear heating rate. The kinetic parameters, E and A can be obtained by plotting $\ln (F(L)/T^2)$ against $1/T$. Various $F(L)$ derived on the basis of theoretical models (Sestak and Berggren 1971) have been examined.

In view of the reasonable order of magnitude of E and A, and the reasonable values of correlation coefficient at a heating rate of 10°C/min, it seems that either a phase boundary reaction or random nucleation and subsequent growth mechanism regulates the thermal dehydration in these crystals. It is difficult to say which of the two mechanisms is the right one.

The dehydration temperatures derived from DTA and TG traces are given in table 2.

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