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DSC studies on the kinetics of decomposition of some Mg-containing borates under high pressures

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Abstract

The dehydration enthalpy ΔH and the activation energy E_a of some Mg-containing borates, viz. macallisterite ($MgO \cdot 3B_2O_3 \cdot 7.5H_2O$), inderite ($2MgO \cdot 3B_2O_3 \cdot 15H_2O$) and kurnakovite ($2MgO \cdot 3B_2O_3 \cdot 15H_2O$) under high pressures (1, 2 and 4 MPa) have been determined by using a DuPont DSC 9900 thermal analyzer. Kinetic parameters for these reactions are discussed and calculated using the Kissinger and simple Ozawa methods.

INTRODUCTION

The Mg-containing borates ($x MgO \cdot y B_2O_3 \cdot z H_2O$) are important substances. The thermo-kinetic feature of some Mg-containing borates under normal pressure were determined in our earlier work. It is necessary to determine their thermal character under high pressure by the DSC method in order to predict their stability and transformation.

SAMPLE PREPARATION

Macallisterite, inderite and kurnakovite were synthesized in our laboratory.

EXPERIMENTAL

A Du Pont differential scanning calorimeter (DSC V2.2A Du Pont 9900) was used for the present kinetic study. The temperature and sensitivity were carefully calibrated under high pressure before the experiments. Heating rates were 5°, 10°, 15° and 20°C min^{-1}. In each run, a sample was placed in an aluminium pan over which a constant current of pure nitrogen gas (50 ml min^{-1}) was passed to remove gas evolved in the decomposition of the sample. The instrument's computer was used on line to collect and store the experimental data.

DATA PROCESSING AND RESULTS

First, the heat flow–temperature curves were obtained after baseline correction (see Figs. 1, 2 and 3).

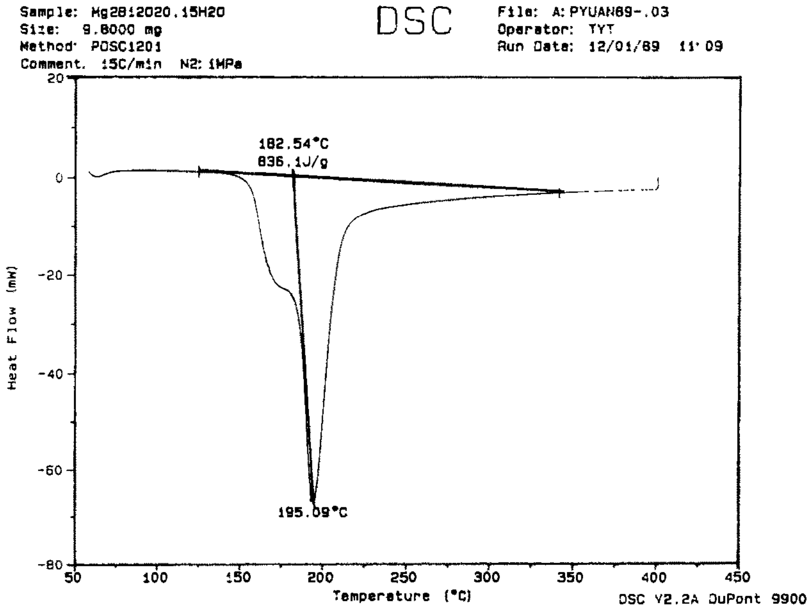

Fig. 1. Heat flow–T curve of macallisterite.

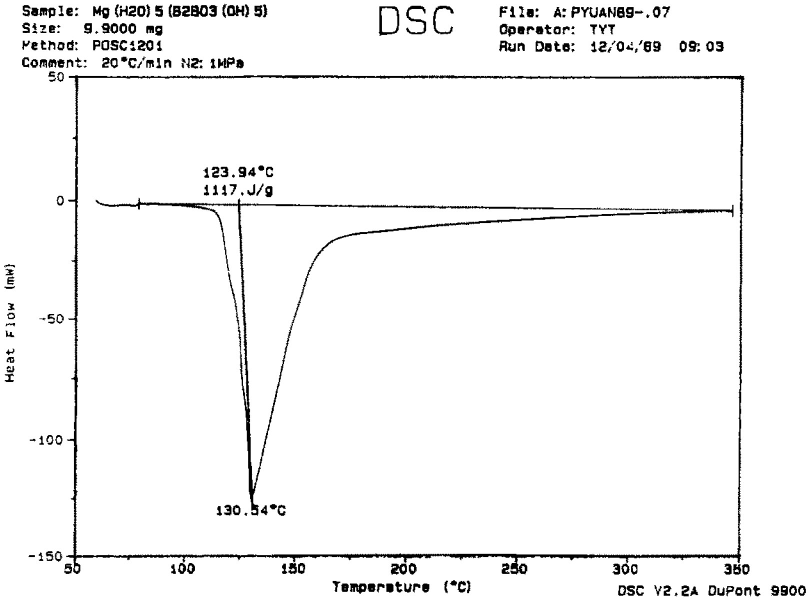

Fig. 2. Heat flow–T curve of inderite.

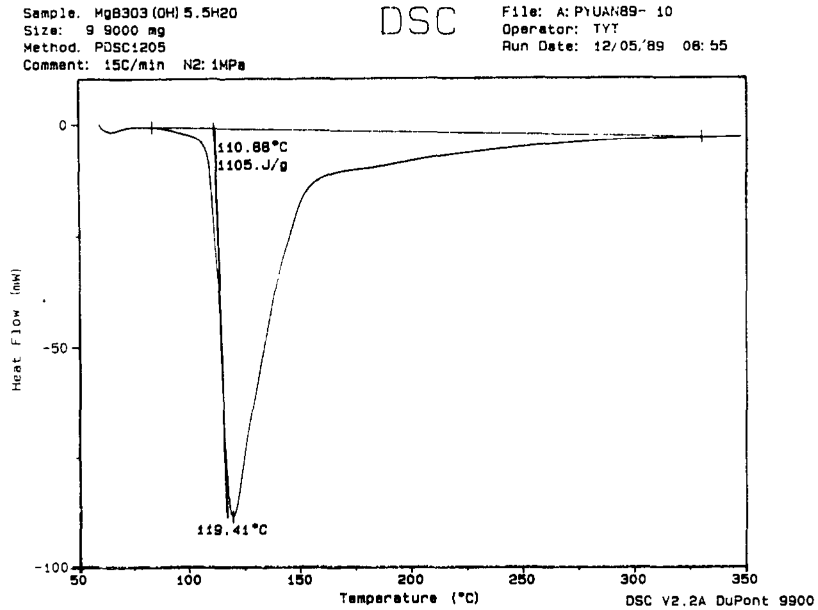

Fig. 3. Heat flow–T curve of kurnakovite.

The dehydration enthalpies, ΔH, of the samples under high pressure were estimated (see Table 1).

Then, the heat flow–temperature curves of the samples under different heating rates (5 °, 10 °, 15 ° and 20 ° C min^{-1}) were recorded (see Figs. 4 and

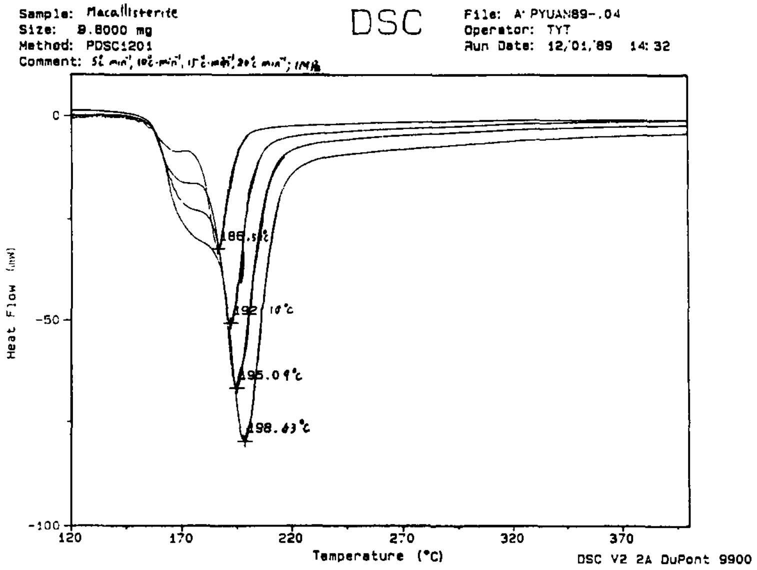

Fig. 4. DSC curves of macallisterite under different heating rates.

TABLE 1

Results for ΔH under different pressures

Macallisterite							Inderite							Kurnakovite						
No.	P (MPa)	Weight (mg)	Heating rate (°C min^{-1})	ΔH (J g^{-1})	$\overline{\Delta H}$ (J g^{-1})	$\overline{\Delta H}$ (kJ mol^{-1})	No.	P (MPa)	Weight (mg)	Heating rate (°C min^{-1})	ΔH (J g^{-1})	$\overline{\Delta H}$ (J g^{-1})	$\overline{\Delta H}$ (kJ mol^{-1})	No.	P (MPa)	Weight (mg)	Heating rate (°C min^{-1})	ΔH (J g^{-1})	$\overline{\Delta H}$ (J g^{-1})	$\overline{\Delta H}$ (kJ mol^{-1})
1	1	9.70	5	839.9	836.7	321.5	13	1	9.60	5	1158.0	1137.8	636.8	25	1	10.00	5	1120.0	1111	621.8
2	1	9.90	10	834.3			14	1	9.60	10	1152.0			26	1	9.80	10	1119.0		
3	1	9.80	15	836.1			15	1	9.90	15	1124.0			27	1	9.90	15	1105.0		
4	1	9.80	20	836.4			16	1	9.90	20	1117.0			28	1	9.80	20	1100.0		
5	2	9.90	5	774.3	729.1	280.2	17	2	10.00	5	948.2	930.9	521.0	29	2	10.00	5	905.9	896.9	502.0
6	2	10.00	10	725.9			18	2	10.00	10	946.0			30	2	10.10	10	901.1		
7	2	10.00	15	687.0			19	2	9.90	15	915.9			31	2	10.00	15	892.9		
8	2	10.10	20	752.2			20	2	10.00	20	913.4			32	2	10.10	20	890.4		
9	4	10.00	5	730.1	662.0	254.4	21	4	10.00	5	794.0	791.8	443.2	33	4	10.10	5	830.1	818.7	458.2
10	4	10.00	10	667.4			22	4	10.00	10	792.9			34	4	10.00	10	818.2		
11	4	10.00	15	625.7			23	4	10.10	15	790.7			35	4	10.10	15	814.0		
12	4	10.10	20	624.9			24	4	10.20	20	789.7			36	4	10.10	20	812.3		

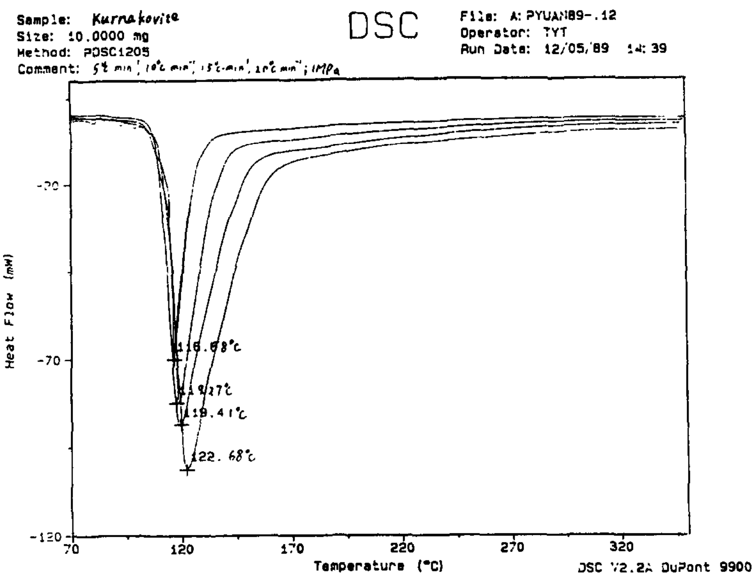

Fig. 5. DSC curves of kurnakovite under different heating rates.

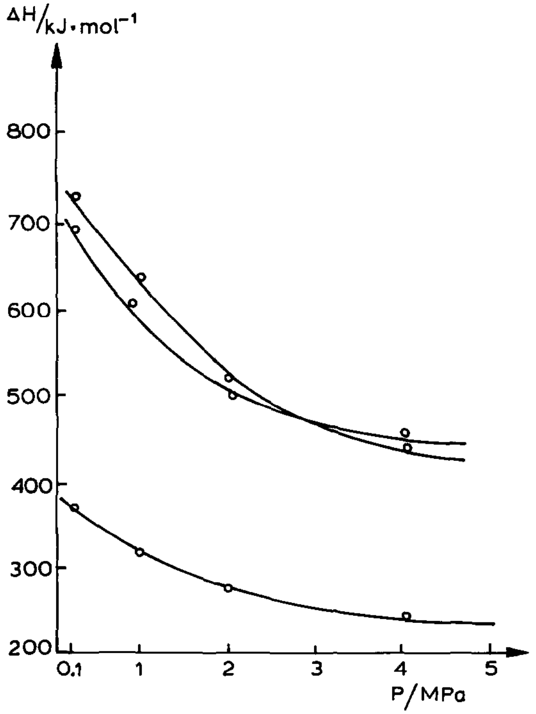

Fig. 6. $\Delta H-P$ curves.

TABLE 2

Data at the different heating rates

Macallisterite							Inderite							Kurnakovite						
No.	P (MPa)	Heating rate (°C min^{-1})	T_m (°C)	$1/T_m$ ×1000	$\ln\left(\frac{\phi}{T_m^2}\right)$	log ϕ	No.	P (MPa)	Heating rate (°C min^{-1})	T_m (°C)	$1/T_m$ ×1000	$\ln\left(\frac{\phi}{T_m^2}\right)$	log ϕ	No.	P (MPa)	Heating rate (°C min^{-1})	T_m (°C)	$1/T_m$ ×1000	$\ln\left(\frac{\phi}{T_m^2}\right)$	log ϕ
37	1	5	186.51	2.1755	−10.6515	0.6990	49	1	5	136.02	2.4440	−10.4188	0.6990	61	1	5	116.68	2.5652	−10.3220	0.6990
38	1	10	192.10	2.1494	−9.9825	1.0000	50	1	10	133.47	2.4593	−9.7132	1.0000	62	1	10	119.27	2.5483	−9.6421	1.0000
39	1	15	195.09	2.1357	−9.5899	1.1761	51	1	15	131.50	2.4713	−9.2980	1.1761	63	1	15	119.41	2.5474	−9.2373	1.1761
40	1	20	198.63	2.1196	−9.3173	1.3010	52	1	20	130.54	2.4771	−9.0056	1.3010	64	1	20	122.68	2.5263	−8.9662	1.3010
41	2	5	185.64	2.1796	−10.6477	0.6990	53	2	5	124.76	2.5131	−10.3630	0.6990	65	2	5	113.34	2.5874	−10.3048	0.6990
42	2	10	191.21	2.1535	−9.9787	1.0000	54	2	10	125.38	2.5092	−9.6730	1.0000	66	2	10	114.64	2.5787	−9.6183	1.0000
43	2	15	194.78	2.1371	−9.5886	1.1761	55	2	15	127.28	2.4973	−9.2770	1.1761	67	2	15	118.27	2.5548	−9.2315	1.1761
44	2	20	199.02	2.1179	−9.3189	1.3010	56	2	20	129.02	2.4865	−8.9980	1.3010	68	2	20	119.06	2.5497	−8.9479	1.3010
45	4	5	184.86	2.1834	−10.6443	0.6990	57	4	5	119.70	2.5455	−10.3374	0.6990	69	4	5	111.00	2.6031	−10.2926	0.6990
46	4	10	191.30	2.1531	−9.9791	1.0000	58	4	10	122.50	2.5275	−9.6585	1.0000	70	4	10	113.18	2.5885	−9.6108	1.0000
47	4	15	195.85	2.1322	−9.5932	1.1761	59	4	15	124.63	2.5140	−9.2637	1.1761	71	4	15	116.99	2.5632	−9.2250	1.1761
48	4	20	197.59	2.1243	−9.3129	1.3010	60	4	20	125.29	2.5098	−8.9794	1.3010	72	4	20	118.86	2.5510	−8.9468	1.3010

TABLE 3

Results for E_a of the samples by different methods

	Macallisterite					
	Kissinger method			Simple Ozawa method		
P (MPa)	1	2	4	1	2	4
E_a (kJ mol^{-1})	202.6	181.84	181.27	199.9	180.2	179.6
r	0.9962	0.9920	0.9970	0.9965	0.9926	0.9972
a	−24.37	−21.87	−21.80	−10.99	−9.903	−9.872
b	42.39	37.08	37.00	24.62	22.31	22.25
	Inderite					
	Kissinger method			Simple Ozawa method		
P (MPa)	1	2	4	1	2	4
E_a (kJ mol^{-1})	347.2	376.9	302.6	324.9	364.6	293.8
r	0.9982	0.9241	0.9954	0.9985	0.9264	0.9956
a	41.76	−45.34	−36.40	17.86	−20.04	−16.15
b	−112.5	103.8	82.31	−42.94	51.17	41.81
	Kurnakovite					
	Kissinger method			Simple Ozawa method		
P (MPa)	1	2	4	1	2	4
E_a (kJ mol^{-1})	285.5	254.0	198.8	277.6	247.5	195.1
r	0.9276	0.9497	0.9710	0.9305	0.9520	0.9727
a	−34.34	−30.55	−23.91	−15.26	−13.61	−10.72
b	77.93	68.92	52.09	39.90	35.98	28.67

Note: a is the slope, r is the linear correlation coefficient.

5). The activation energies of decomposition of the samples were estimated by the methods of Kissinger [4] and the simple Ozawa [2,3] methods (Tables 2 and 3).

Formula of Kissinger

$$\ln(\phi/T_m^2) = \ln(AR/E_a) - E_a/R(1/T_m)$$

Simple formula of Ozawa

$$\log \phi = -0.457E_a/(RT_m) + C$$

In the formula, ϕ is the heating rate and T_m is the peak temperature.

CONCLUSIONS

1. Our experiments show that the ΔH values of the three borates decrease with increasing pressure (see Fig. 6).

2. The activation energies E_a increase to maxima and then decrease again as the pressure increases (see Fig. 7).

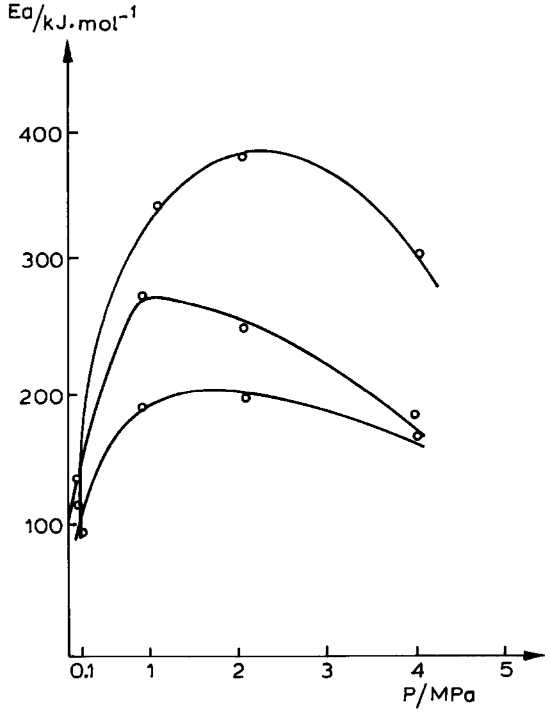

Fig. 7. $E_a - P$ curves.

3. At 1 MPa and 2 MPa pressure: ΔH(inderite) > ΔH(kurnakovite) > ΔH(macallisterite); at 4 MPa pressure: ΔH(kurnakovite) > ΔH(inderite) > ΔH(macallisterite).

4. At high pressure (1, 2 and 4 MPa): E_a (inderite) > E_a(kurnakovite) > E_a(macallisterite).

Note: ΔH and E_a values at normal pressure are results from our previous work.

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