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DSC studies on the kinetics of decomposition of some Mg-containing borates under normal pressure

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Abstract

The dehydration enthalpy ΔH and the apparent activation energy E_a of some Mg-containing borates viz. macallisterite ($MgO \cdot 3B_2O_3 \cdot 7 \cdot 5H_2O$), inderite ($2MgO \cdot 3B_2O_3 \cdot 15H_2O$) and kurnakovite ($2MgO \cdot 3B_2O_3 \cdot 15H_2O$) under normal pressure have been determined by using a Du Pont DSC 9900 (US) thermal analyzer. Kinetic parameters for these reactions are calculated using the method of Kissinger and the simple Ozawa method.

INTRODUCTION

The Mg-containing borates ($x MgO \cdot y B_2O_3 \cdot z H_2O$) are important types of borate. It is necessary to determine their thermo-kinetic features by DSC in order to predict their stability and transformation. We have studied 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 normal pressure. The dehydration enthalpy ΔH and activation energy E_a of some Mg-containing borates were obtained from non-isothermal calorimetric techniques.

SAMPLE PREPARATION

Macallisterite, inderite and kurnakovite were synthesized using analytically pure reagents. The amounts of reagents added and the pH value of the mixture were controlled according to the chanza (i.e. mixing) principle [1].

TABLE 1

Results of chemical analysis

	MgO (%)	B_2O_3 (%)	H_2O (%)	Total (%)
Macallisterite	10.50	53.80	35.63	99.93
Inderite	14.44	37.28	48.28	100.00
Kurnakovite	14.49	37.23	48.23	99.95

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Processes such as dissolution, heating, evaporation, diluting, freezing and crystallization were used. Compositions of the synthetic borates were confirmed by chemical analysis (see Table 1), X-ray analysis (see Figs. 13–15) and scanning electron microscope analysis (see Figs. 16–18).

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 before the experiments. Indium (purity > 99.9%) and tin (purity > 99.9%) were used as the primary standard substances. Heating rates were 5°, 10°, 15° and 20°C min^{-1}. In each run, a sample was placed as a shallow layer in an aluminium pan, over which a constant current of pure nitrogen gas (50 ml min^{-1}) was passed to remove the gas evolved by decomposition of the sample. In order to ensure identical conditions, three runs were carried out consecutively after prolonged stabilization. Sieving of the dried powder provided specimens of uniform size (0.0425–0.0025 mm).

The computer of the DSC V2.2A Du Pont 9900 was used on line to collect and store experimental data amounting to about 2000–4000 points. The stored data were then processed with an Apple-II computer using a special program developed by us.

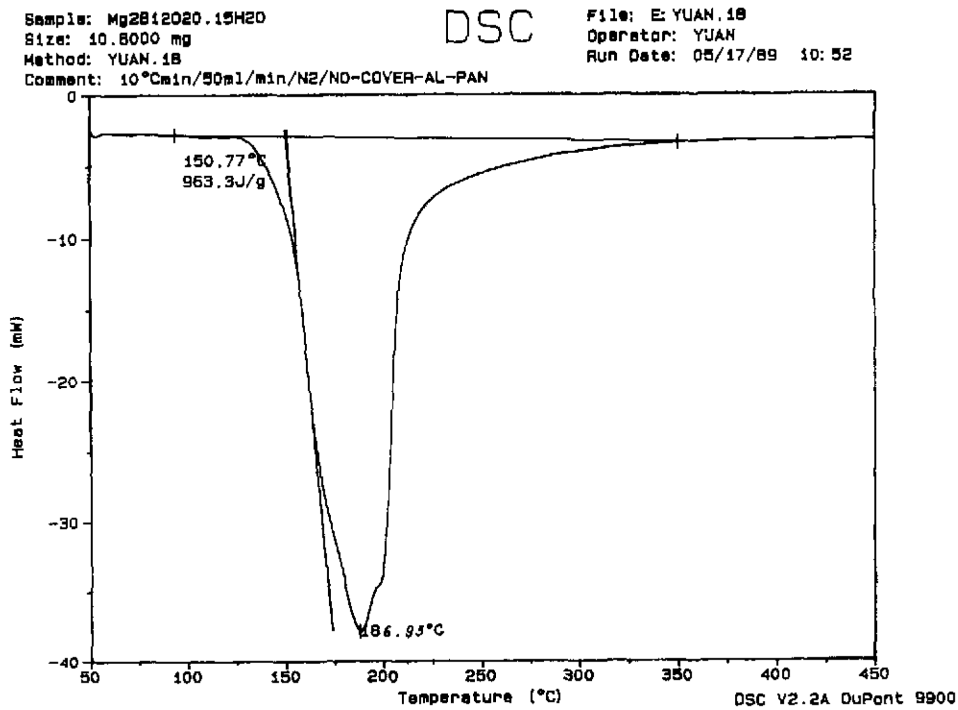

Fig. 1. The heat flow–*T* curve of macallisterite.

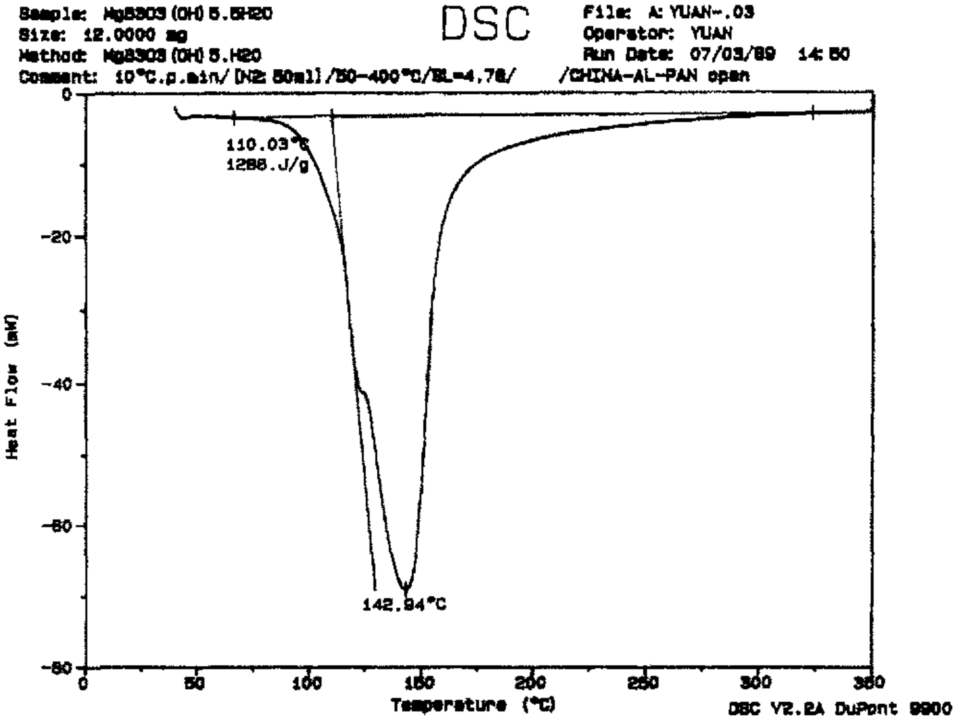

Fig. 2. Heat flow–T curve of inderite.

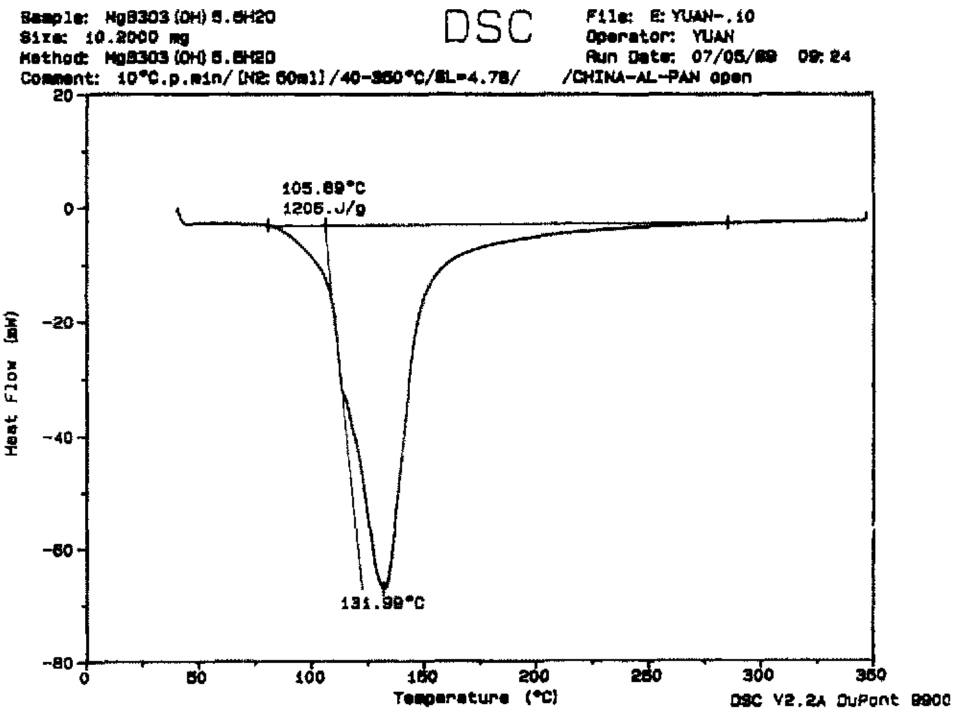

Fig. 3. Heat flow–T curve of kurnakovite.

TABLE 2

Results for ΔH of Mg-containing borates

Sample	No.	N_2(g) (ml min^{-1})	Heating rate (°C min^{-1})	ΔH (J g^{-1})	Mean ΔH (J g^{-1})	Mean ΔH (kJ mol^{-1})
Macallisterite	1	50	10	960.2		
	2	50	10	963.3	961.8	369.6
	3	50	10	961.9		
Inderite	4	50	10	1288		
	5	50	10	1287	1287	720.4
	6	50	10	1286		
Kurnakovite	7	50	10	1206		
	8	50	10	1207	1206	675.0
	9	50	10	1205		

DATA PROCESSING AND RESULTS

The data processing consisted of two steps. First, the heat flow–temperature curves were given after baseline correction (see Figs. 1, 2 and 3). The dehydration enthalpies ΔH of the samples were estimated (see Table 2).

Then the heat flow–temperature curves of the samples under different heating rates (5°, 10°, 15° and 20°C min^{-1}) were obtained (see Figs. 4, 7 and 10; Table 3). The activation energies of the decomposition of the

TABLE 3

Data for different heating rates

No.	Heating rate (°C min^{-1})	Peak temperature (°C)	$(1/T_m)\times1000$ (K)	$\ln(\phi/T_m^2)$	$\log(\phi)$
Macallisterite					
11	5	174.94	2.2317	−10.601	0.6990
12	10	186.95	2.1734	−9.960	1.0000
13	15	192.22	2.1488	−9.578	1.1761
14	20	198.02	2.1224	−9.315	1.3010
Inderite					
15	5	135.24	2.4486	−10.415	0.6990
16	10	142.94	2.4033	−9.759	1.0000
17	15	148.55	2.3714	−9.381	1.1761
18	20	154.08	2.3407	−9.119	1.3010
Kurnakovite					
19	5	124.99	2.5117	−10.364	0.6990
20	10	131.99	2.4683	−9.706	1.0000
21	15	136.17	2.4431	−9.321	1.1761
22	20	139.89	2.4211	−9.051	1.3010

TABLE 4

Results for E_a of the samples by different methods

	Macallisterite			Inderite			Kurnakovite		
	E_a (kJ mol^{-1})	r	a	E_a (kJ mol^{-1})	r	a	E_a (kJ mol^{-1})	r	a
K's method	99.29	0.9978	−11.94	100.7	0.9937	−12.12	121.7	0.9992	−14.64
O's method	101.6	0.9981	−5.585	102.3	0.9945	−5.624	122.0	0.9993	−6.709

Note: a is the slope; r is the linear correlation coefficient. K = Kissinger; O = simplified Ozawa.

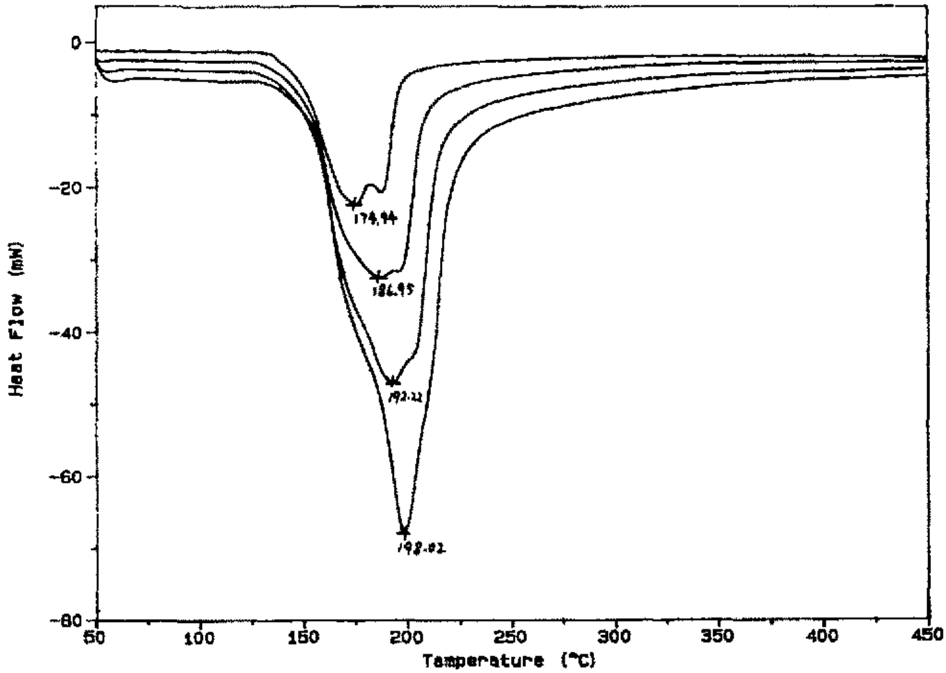

Fig. 4. DSC curves of macallisterite under different heating rates.

samples were estimated by the Kissinger [2,6] and simple Ozawa [3,4] methods (see Figs. 5, 6, 8, 9, 11 and 12; Table 4).

Formula of Kissinger

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

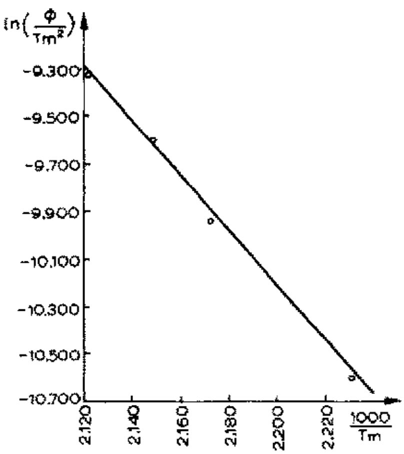

Fig. 5. $\ln(\phi/T_m^2)$–$1/T_m$ curve of macallisterite.

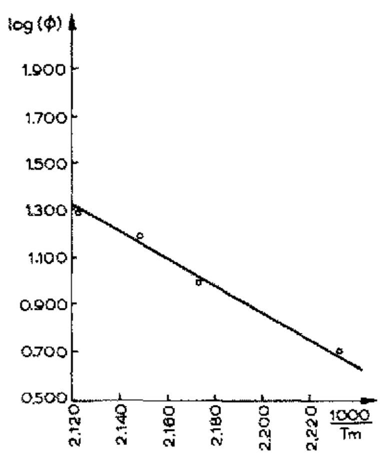

Fig. 6. Log ϕ–$1/T_m$ curve of macallisterite.

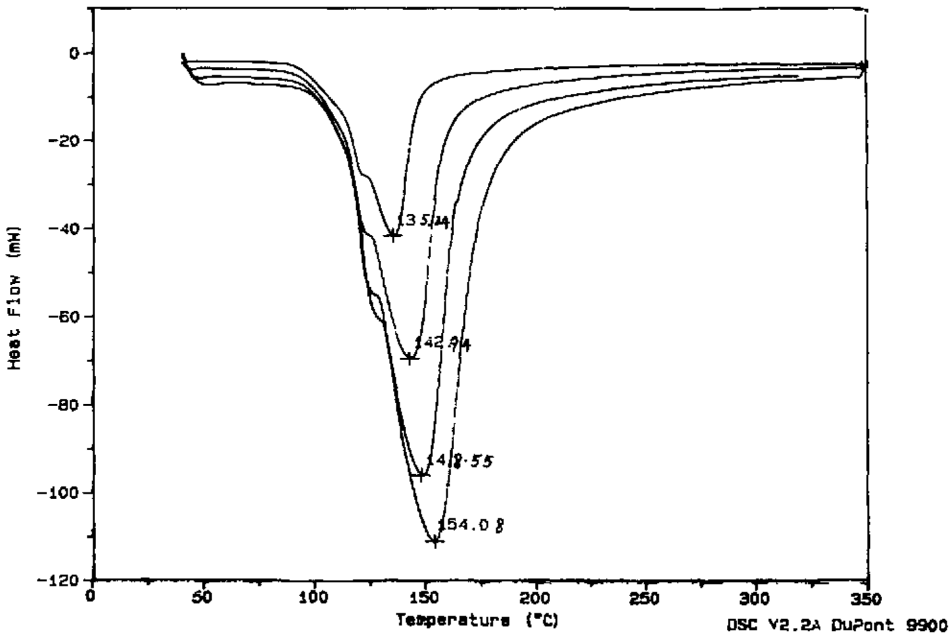

Fig. 7. DSC curves of inderite under different heating rates.

Simple formula of Ozawa

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

In the formulae, ϕ is the heating rate, T_m is the peak temperature and R is the gas constant.

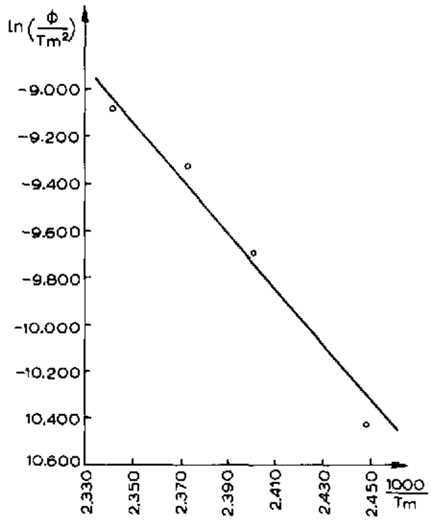

Fig. 8. Ln(ϕ/T_m^2)–$1/T_m$ curve of inderite.

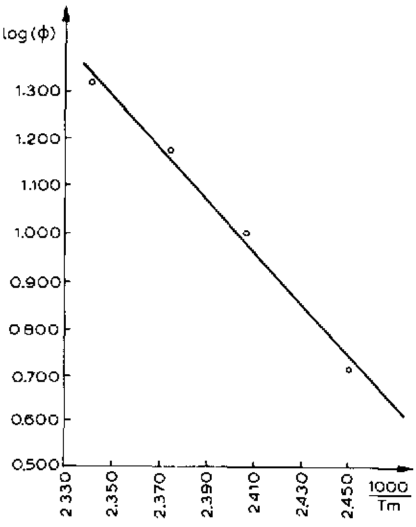

Fig. 9. Log ϕ–$1/T_m$ curve of inderite.

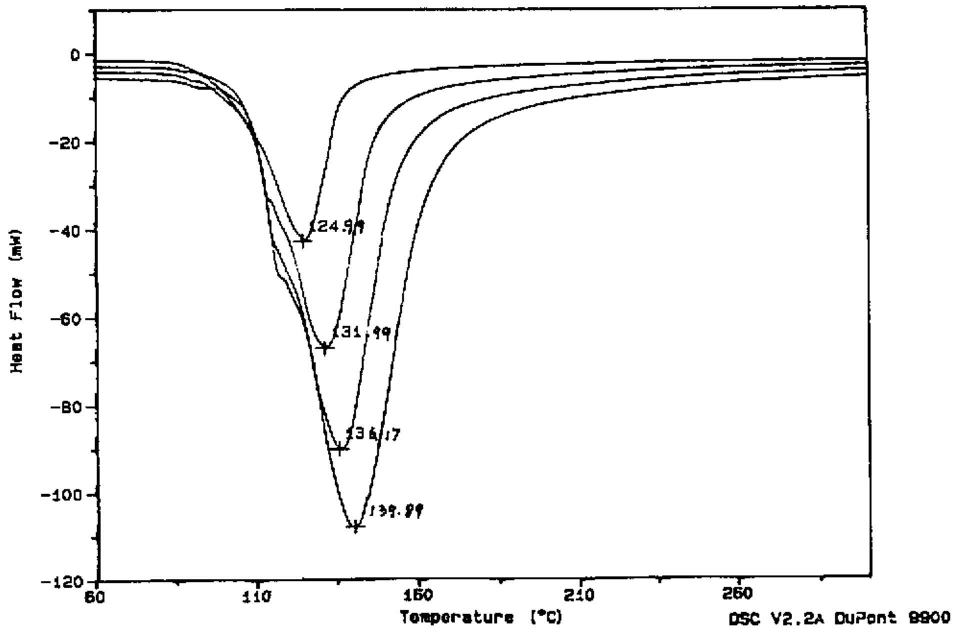

Fig. 10. DSC curves of kurnakovite under different heating rates.

CONCLUSIONS

1. Experiments show that the dehydration enthalpies increase in the series ΔH(macallisterite) < ΔH(kurnakovite) < ΔH(inderite) under normal pressure.

2. Experiments also show that the activation energies of the borates increase in the series E_a(macallisterite) < E_a(inderite) < E_a(kurnakovite) under normal pressure.

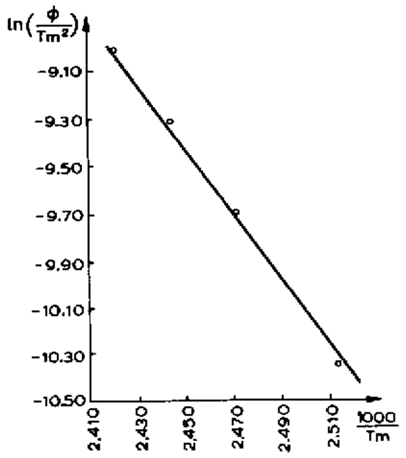

Fig. 11. Ln(ϕ/T_m^2)–$1/T_m$ curve of kurnakovite.

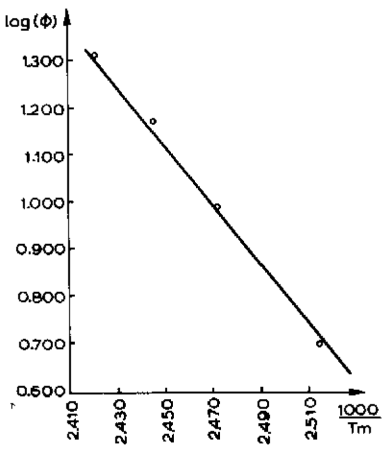

Fig. 12. Log ϕ–$1/T_m$ curve of kurnakovite.

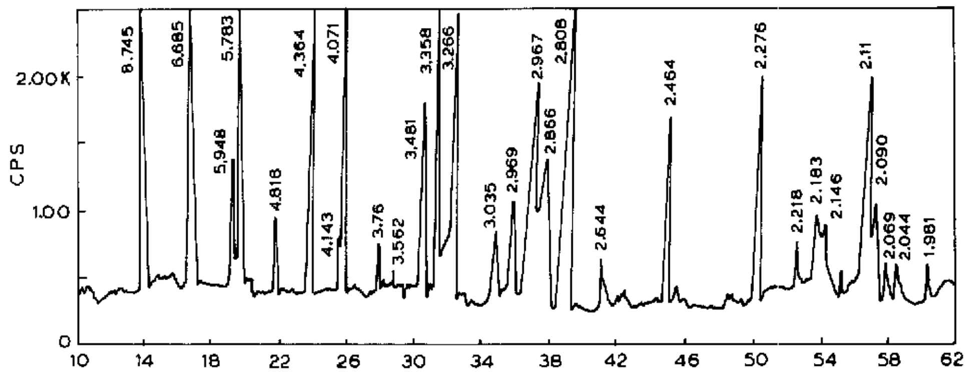

Fig. 13. X-ray analysis of macallisterite.

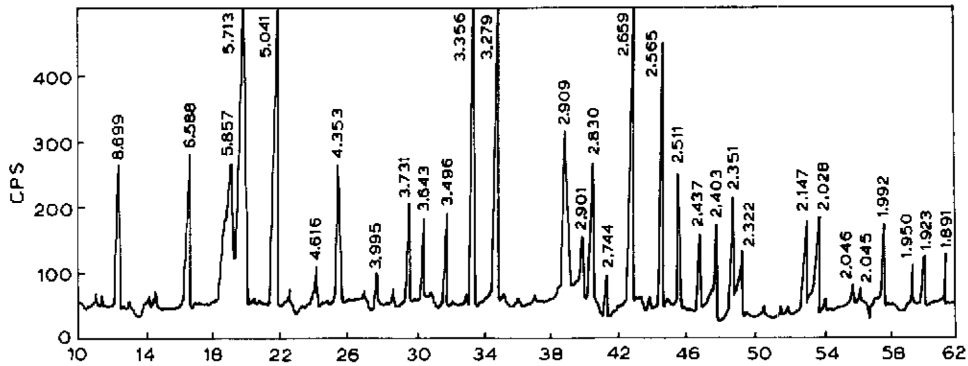

Fig. 14. X-ray analysis of inderite.

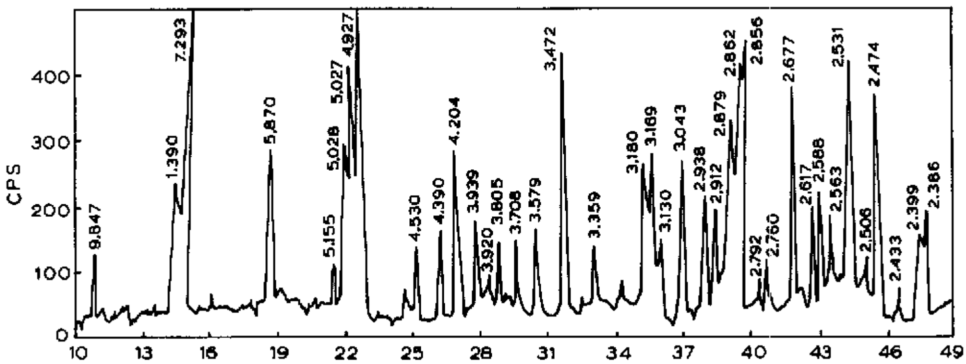

Fig. 15. X-ray analysis of kurnakovite.

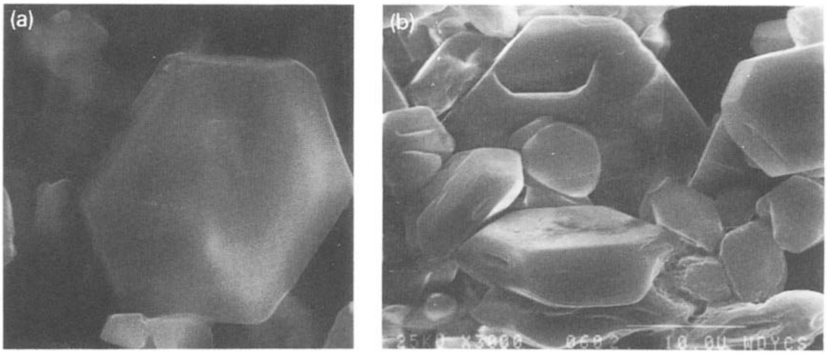

Fig. 16. Scanning electron micrograph of macallisterite. Original magnification: left, ×7200; right, ×3000.

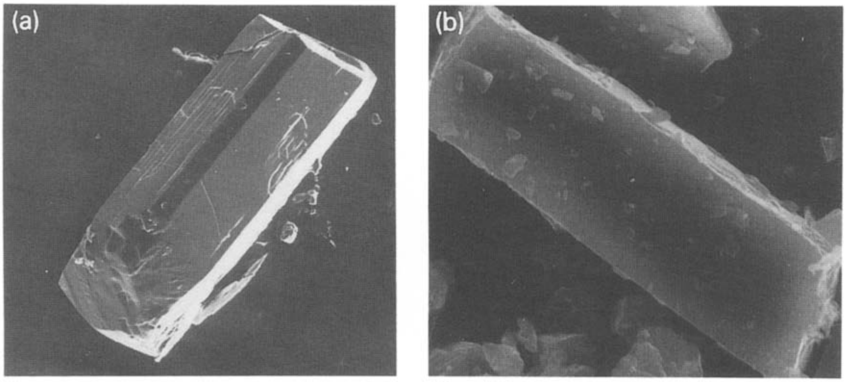

Fig. 17. Scanning electron micrograph of inderite. Original magnification: left, ×720; right, ×500.

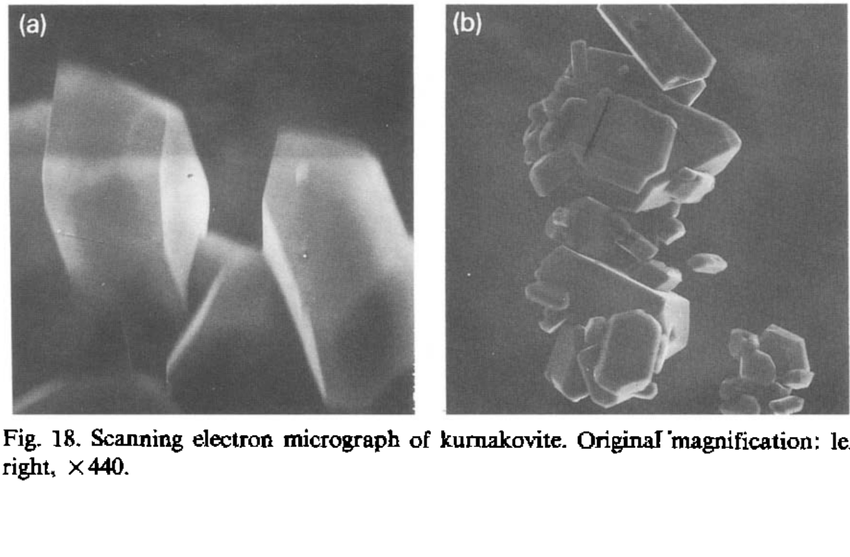

Fig. 18. Scanning electron micrograph of kurnakovite. Original magnification: left, ×3600; right, ×440.

3. The structures of Mg-containing borates are complex. They can be formulated as sp^2 hybrid orbital or sp^3 hybrid orbital structures, which are, respectively, the layer structure or the island structure. Macallisterite has the layer structure, and the chemical formula is $[B_3B_3O_9(OH)_2]$ [5]. Inderite and kurnakovite have the island structure, and their chemical formula is $[B_2BO_3(OH)_5]$ [5]. We obtain the results ΔH(island) > ΔH(layer), E_a(island) > E_a(layer) under normal pressure. This sequence is attributable to the hydrogen bonds between the layers of the layer structure.

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