Thermochimica Acta, 233 (1994) 211–218
Elsevier Science B.V., Amsterdam
SSDI 0040-6031(93)01480-Q

Synthesis and properties of dimagnesium hexaborate heptadecahydrate

Li Jun, Song Peng-Sheng * and Sun Bai

The Institute of Salt Lakes, Academia Sinica, Xining (People's Republic of China)

(Received 24 June 1993; accepted 5 July 1993)

Abstract

A magnesium borate compound $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ has been synthesized and its structure studied by IR and Raman spectroscopy as well as by thermal analysis. The structural formula of this compound was $Mg[B_3O_3(OH)_5] \cdot 6H_2O$. Its solubility in pure water at 25°C, refractive index, thermodynamic properties, and X-ray powder diffraction data are reported.

INTRODUCTION

There are many kinds of magnesium borates, both natural and synthetic. The ternary system $MgO–B_2O_3–H_2O$ has been studied at different temperatures by several authors [1, 2]. It has been found that different magnesium borates can exist in different temperature and pH ranges. Kesans [3] reported that Gode had obtained a magnesium borate $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ (in abbreviated form 2:3:17) prepared by precipitating boron from aqueous solution by using MgO; the refractive indices of this compound were Ng = 1.502 and Np = 1.486; the thermogravimetric (TG) curve of this compound indicated that it lost 12 water molecules between 65 and 70°C. About thirty years later, Gode et al. [4] investigated the IR spectrum of this compound again and compared it with those of inderite ($2MgO \cdot 3B_2O_3 \cdot 15H_2O$) and kaliborite ($K_2O \cdot MgO \cdot 3B_2O_3 \cdot 9H_2O$). They believed that the structural unit of this compound is $[B_3O_3(OH)_5]^{2-}$, its structural formula being $Mg[B_3O_3(OH)_5] \cdot 6H_2O$. However, the method of synthesis used was not reported in either of these two studies. We discovered a way of synthesizing this compound when investigating the magnesium borate system [5, 6]. Its structure has been studied using IR and Raman spectra, and thermal analysis, and its properties are reported here.

* Corresponding author.

EXPERIMENTAL

Synthesis

50.0 g $MgSO_4 \cdot 7H_2O$ (GR) and 25.0 g of $NaBO_2 \cdot 4H_2O$ (AR) were dissolved completely in 300.0 cm^3 of deionized water with heating. 35.0 g of $Na_2B_4O_7 \cdot 10H_2O$ (GR) was dissolved in 100.0 cm^3 of deionized water and heated to obtain a clear solution. The latter aqueous solution was then added to the former and the mixed solution was placed in a sealed glass tube and put in a water bath at 25°C, and stirred for a few hours. The product was filtered, washed two or three times with deionized water, and the solid was stored in a desiccator until constant weight was attained.

Method

Chemical analyses were performed according to the literature method [7]. The solubility of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ in water at 25°C was measured in a sealed glass equilibrium tube placed in a water bath controlled at 25 ± 0.05°C. Infrared spectra were recorded on a Perkin-Elmer 683 spectrometer with samples prepared as KBr pellets. Raman spectra was recorded on a SPEX1403 spectrometer using an Ar^+ beam laser (5145 nm at 200 nW), the samples being placed in pyrex tubes. DG and DTA measurements were carried out on a DuPont 1090 thermal analyzer in flowing N_2(40 $cm^3\,min^{-1}$) at a heating rate of 10°C min^{-1}. DSC was performed on a Setaram DSC111 in flowing N_2 (50 $cm^3\,min^{-1}$) with a heating rate of 5°C min^{-1}. X-ray powder diffraction patterns were recorded on a Rigaku Model D/MAX-III-B diffractometer operation at 40 kV and 30 mA, using a copper target. The standard enthalpy of formation of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ can be obtained from the following thermodynamic cycle

$$2MgO \cdot 3B_2O_3 \cdot 17H_2O \rightarrow 2MgO + 6H_3BO_3 + 8H_2O \quad \Delta H_m \tag{1}$$

$$2MgO \cdot 3B_2O_3 \cdot 17H_2O + 4HCl + 217.4H_2O \rightarrow 2MgCl_2 + 6H_3BO_3 + 227.4H_2O \quad \Delta H_1 \tag{2}$$

$$2MgO + 4HCl + 217.4H_2O \rightarrow 2MgCl_2 + 219.4H_2O \quad \Delta H_2 \tag{3}$$

$$6H_3BO_3 + 8H_2O + 2MgCl_2 + 219.4H_2O \rightarrow 2MgCl_2 + 6H_3BO_3 + 227.4H_2O \quad \Delta H_3 \tag{4}$$

About 5.0000×10^{-4} mol of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ was dissolved in

100.0 cm^3 of 0.997 mol l^{-1} HCl solution (4HCl, 217.4H_2O). About 1.0000×10^{-3} mol of MgO was dissolved in 100.0 cm^3 of 0.997 mol l^{-1} HCl solution, and then about 3.0000×10^{-3} mol of H_3BO_3 was dissolved in the former solution. Because the amount of H_2O (about 4.0000×10^{-3} mol) calculated according to eqn. (1) is very small, neglecting the dilution enthalpy of the mixed solution has minimal influence on the precision of the results. The uncertainty of the thermochemical experiment is less than 0.5%. All calorimetric experiments were performed on a home-made isoperibol reaction calorimeter [8]. From the above equations

$$\Delta H_m = 2\Delta H_2 + 6\Delta H_3 - \Delta H_1 \qquad (5)$$

and the standard enthalpy of formation of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ is

$$\Delta_f H^{\ominus}_{298} = 2\Delta_f H^{\ominus}_{MgO(cry),298} + 6\Delta_f H^{\ominus}_{H_3BO_3(cry),298} + 8\Delta_f H^{\ominus}_{H_2O(liq),298} - \Delta H_m \qquad (6)$$

RESULTS AND DISCUSSION

Structure

Chemical analysis results of five synthetic $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ samples are reported in Table 1. The IR spectrum of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ exhibited the following absorptions: 3665(m), 3390(w), 3220(w), 2560(m), 2300(w), 1670(s), 1470(w), 1425(s), 1368(w), 1315(s), 1255(w), 1160(vs), 1020(w), 950(m), 860(s), 805(m), 750(m), 690(m), 440(s), 370(vs), 310(m), 260(w) and 220(vs) cm^{-1}. Comparisons of the IR spectrum with those of other magnesium borates with the same mole ratio of $MgO:B_2O_3$ are displayed in Fig. 1. It can be seen that IR spectrum of our synthetic compound is idetnical to that of the compound obtained by Gode and similar to those of inderite and kurnakovite [9]. These three compounds should have the same structure unit. The Raman spectrum of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ is shown in Fig. 2. Unfortunately, there are no

TABLE 1

Chemical analyses of synthetic $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ (wt.%)

No.	MgO	B_2O_3	H_2O	Mole ratio	pH of soln.
1	13.53	35.28	51.19	2:3.02:16.93	
2	13.51	34.93	51.56	2:2.99:17.08	9.34
3	13.49	35.06	51.45	2:3.01:17.07	
4	13.51	35.08	51.41	2:3.01:17.03	9.20
5	13.59	35.01	51.00	2:2.98:17.00	9.00
Calc. value	13.53	35.06	51.41	2:3.00:17.00	

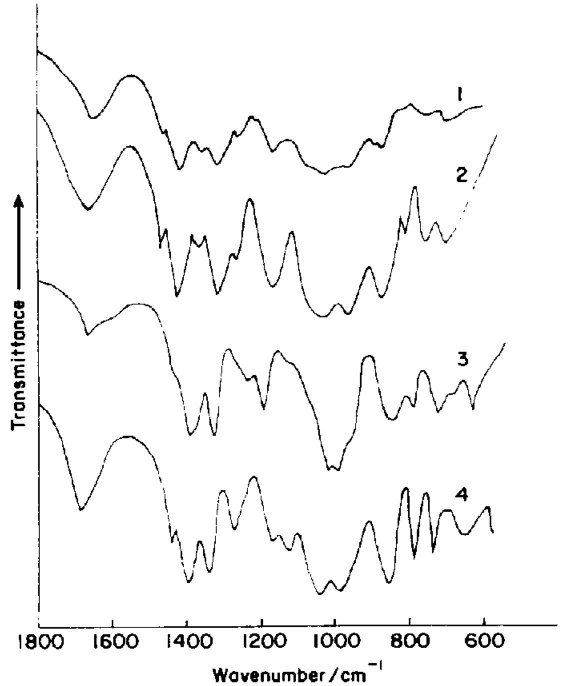

Fig. 1. IR spectra of magnesium borates: 1, Gode et al. [4]; 2, present work; 3, kurnakovite; 4, inderite.

published Raman spectra available for comparision. Thermal analyses (Fig. 3) indicate three peaks between room temperature and 1200°C. The first endothermic peak of dehydration appears at 110.5°C with a maximum slope at 111.5°C. The weight loss (46.9%) corresponds to the loss of 17 water molecules and can be compared with the calculated value of 51.41%. The second exothermic peak corresponds to recrystallization of the product formed after dehydration, and the third endothermic peak represents the melting point [3]. The loss of the 12 water molecules does not appear on the TG curve. The enthalpy of dehydration of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ determined by DSC is 746.78 kJ mol^{-1}. Therefore, $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ has the same structure unit, $[B_3O_3(OH)_5]^{2-}$, as inderite and kurnakovite, and its structural formula can be written as $Mg[B_3O_3(OH)_5] \cdot 6H_2O$.

Properties

The solubility of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ in water at 25°C is 0.420% (weight percent of anhydrous salt); inderite and kurnakovite are 0.297% and 0.321% soluble, respectively [10]. Table 2 gives X-ray powder

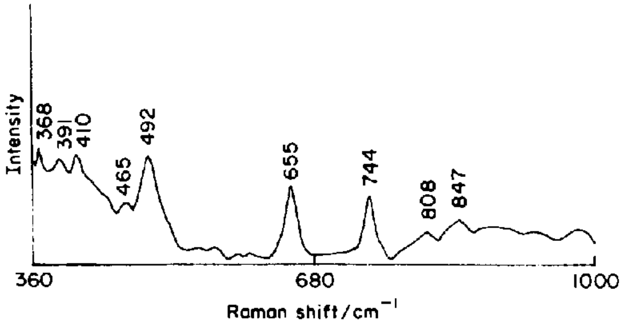

Fig. 2. Raman spectrum of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$.

diffraction data for $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ in comparison with inderite and kurnakovite [11]. These three magnesium borates have the same structural unit, but they do not have the same solubility in water because their crystal structures are different. Moreover, there is no transition for $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ to other magnesium borates more than a month after the solubility experiment (confirmed by IR spectroscopy). Thus, $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ can be considered to be a congruent compound.

The refractive indices of a $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ crystal are Ng = 1.504, Np = 1.467: this is consistent with Gode's results.

As described above, the standard enthalpy of formation of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ can be calculated from eqns. (5) and (6). The solution enthalpies of MgO and H_3BO_3 are taken from an earlier paper [12]: $\Delta H_2 = -73.472\ \mathrm{kJ\ mol^{-1}}$; $\Delta H_3 = 21.933\ \mathrm{kJ\ mol^{-1}}$. The solution enthalpies of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ in $100.0\ \mathrm{cm^3}$ of $0.997\ \mathrm{mol\ l^{-1}}$ HCl solution are shown in Table 3. The standard enthalpies of formation of MgO, H_3BO_3 and H_2O are taken from Weast [13]. Thus

$$\Delta H_m = 2\Delta H_2 + 6\Delta H_3 - \Delta H_1 = -69.870\ \mathrm{kJ\ mol^{-1}}$$

$$\Delta_f H^{\ominus}_{298} = -9986.12\ \mathrm{kJ\ mol^{-1}}$$

The standard Gibbs free energy of formation of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ can be calculated separately according to Bassett [14] and Mattigod [15]. The average value is $-8977.92\ \mathrm{kJ\ mol^{-1}}$. The standard entropy of formation of this compound $\Delta_f S^{\ominus}_{298}$ is $-3381.52\ \mathrm{J\ mol^{-1}\ K^{-1}}$. Finally, the standard mole entropy $S^{\ominus}_{298}$ is

$$S^{\ominus}_{298} = 2S^{\ominus}_{Mg(cry),298} + 6S^{\ominus}_{B(cry),298} + 17S^{\ominus}_{H_2(g),298} + 14S^{\ominus}_{O_2(g),298} + \Delta_f S^{\ominus}_{298}$$

$$= 2439.45\ \mathrm{J\ mol^{-1}\ K^{-1}}$$

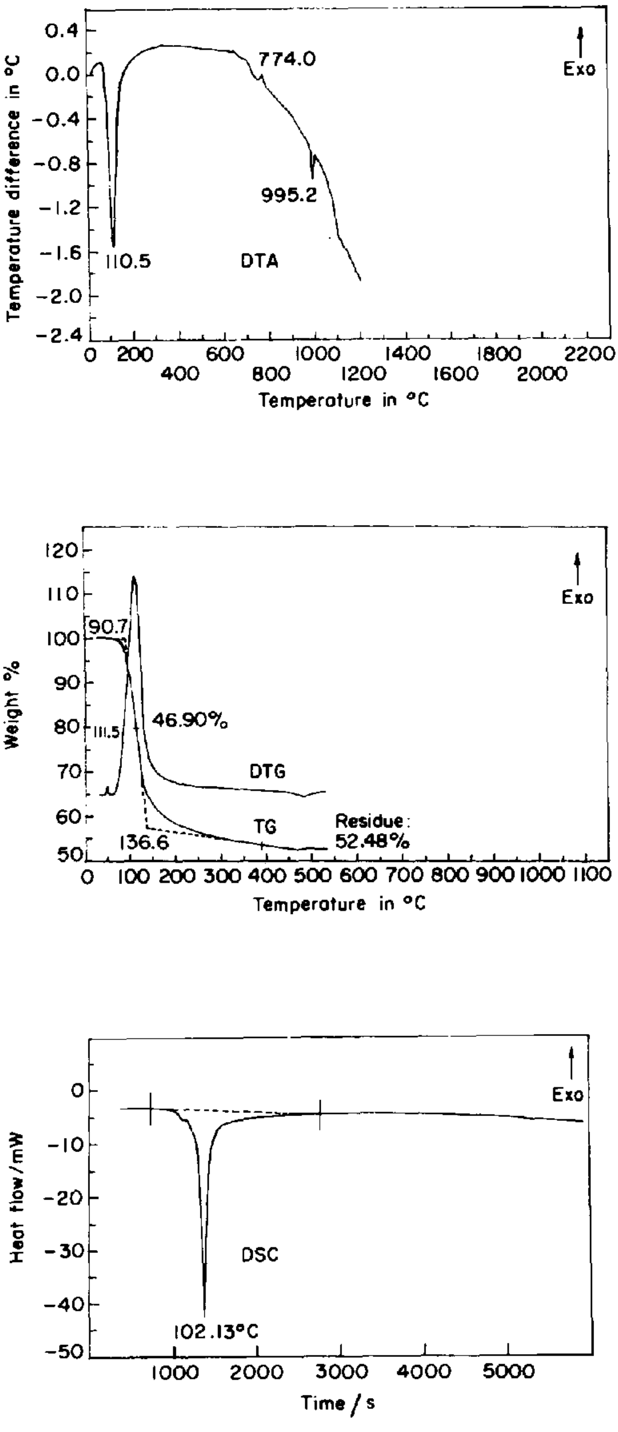

Fig. 3. Thermal analyses of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$.

TABLE 2

X-ray powder diffraction data of magnesium borates

$2MgO \cdot 3B_2O_3 \cdot 17H_2O$		Inderite		Kurnakovite	
d/Å	I/I_0	d/Å	I/I_0	d/Å	I/I_0
11.168	100	6.55	70	7.21	100
6.953	40	5.69	100	5.84	50
6.802	40	5.02	90	4.95	100
5.583	52	3.74	50	3.47	70
5.460	30	3.36	100	3.15	70
5.015	72	2.94	100	3.05	60
4.362	32	2.67	70	2.85	80
4.224	34	2.55	70	2.67	50
3.729	33	2.51	50	2.47	60
3.373	33	2.44	50		
3.317	41	2.35	70		
3.196	44	2.14	70		
3.154	43	1.68	70		
2.813	40	1.49	50		

TABLE 3

The solution enthalpy of $2MgO \cdot 3B_2O_3 \cdot 17H_2O$ in 100.0 cm^3 of 0.997 mol l^{-1} HCl solution

No.	$n \times 10^4$/mol	ΔH/kJ mol^{-1}	Error/%
1	4.9598	54.610	0.16
2	4.9804	54.639	0.21
3	5.0781	54.304	−0.40
4	5.0479	54.683	0.29
5	5.0593	54.382	−0.26
Av.		54.524	

ACKNOWLEDGMENTS

We gratefully acknowledge Professors Qu Sh.Sh., Song Zh.H. and Qu J.N. (University of Wuhan) for their kind help when L.J. was working in their thermochemistry laboratory, Ms. Xu K.F. for the IR spectra, Mr. Yang B. for the X-ray powder diffraction data, and Mr. Wang H.D. for the DSC analyses.

REFERENCES

1 J.B. Famer, Metal Borates, in H.J. Emelius and A.G. Sharpe (Eds.), Advances in Inorganic Chemistry and Radiochemistry, Vol. 25, Academic Press, London, 1982, p. 187.

2 H.L. Silcock (Ed.), Solubilities of Inorganic and Organic Compounds, Pergamon Press, Oxford, 1979.
3 A. Kesans, Synthesis of Borates in Aqueous Solution and their Investigation, Science Press, Beijing, 1965 (in Chinese).
4 H. Gode, I. Majore and V.I. Borisenkov, Latv. PSR Zinst. Akad. Vestis, Khim. Ser., 5 (1981) 601.
5 P.Sh. Song, X.H. Du and B. Sun, Kexue Tongbao, 32 (1987) 1492 (in Chinese).
6 P.Sh. Song and H.An. Fu, Wuji Huaxue Xuebao, 7 (1991) 344 (in Chinese).
7 The Institute of Salt Lakes, Academia Sinica, P.R. of China, The Analytical Methods of Salt and Brine, 2nd edn., Science Press, Beijing, 1989.
8 C.X. Wang, Zh.H. Song, W.G. Xiong and Sh.Sh. Qu, Wuli Huaxue Xuebao, 7 (1991) 586 (in Chinese).
9 S.D. Ross, in V.C. Farmer (Ed.), The Infrared Spectra of Minerals, Adlard and Son Ltd., Dorking, Surrey, UK, 1974.
10 F.X. Zhang, Y. Ma and Zh.Zh. Guo, J. Northwest University, 20 (1990) 158 (in Chinese).
11 F.M. He, Sh.Sh. Liu et al., Handbook of Identification Methods for Salts and Minerals, Chemical Industry Press, Beijing, 1988.
12 J. Li, Sh.Y. Gao, G.N. Qu and S.Sh. Qu, Yingyong Huaxue, 1993, 10(3) (1993) 12 (in Chinese).
13 R.C. Weast, (Ed.), CRC Handbook of Chemistry and Physics, 61st edn., CRC Press, Boca Raton, FL, 1980.
14 R.L. Bassett, Ph.D. Dissertation, Stanford University, USA, 1976.
15 S.V. Mattigod, Soil Sci. Soc. Am. J., 47 (1983) 654.