

Synthesis, characterization, and thermochemistry of a new form of $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$

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Abstract

A new magnesium borate, $\beta\text{-}2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$, has been synthesized by the method of phase transformation of double salt and characterized by XRD, IR, and Raman spectroscopy as well as by TG. The structural formula of this compound was $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5]\cdot 6\text{H}_2\text{O}$. The enthalpy of solution of $\beta\text{-}2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$ in approximately 1 mol dm^{-3} HCl was determined. With the incorporation of the standard molar enthalpies of formation of $\text{MgO}(\text{s})$, $\text{H}_3\text{BO}_3(\text{s})$, and $\text{H}_2\text{O}(\text{l})$, the standard molar enthalpy of formation of $-(10256.39 \pm 4.93)\text{ kJ mol}^{-1}$ of $\beta\text{-}2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$ was obtained. Thermodynamic properties of this compound was also calculated by group contribution method. © 2004 Elsevier B.V. All rights reserved.

Keywords: $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$; Synthesis; Characterization; Standard molar enthalpy of formation

1. Introduction

There are many kinds of magnesium borates, both natural and synthetic. Up to now, four hydrated magnesium borates containing the polyborate anion of $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ are found. They are $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 13\text{H}_2\text{O}$, $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 15\text{H}_2\text{O}$ (inderite), $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 15\text{H}_2\text{O}$ (kurnakovite), and $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$ [1]. Of these, inderite and kurnakovite are the two forms of $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 15\text{H}_2\text{O}$. They have the same structural form of $\text{Mg}[\text{B}_3\text{O}_3(\text{OH})_5](\text{H}_2\text{O})_4\cdot \text{H}_2\text{O}$, and contain the same six membered ring of $[\text{B}_3\text{O}_3(\text{OH})_5]^{2-}$ group, which is composed of one BO_3 planar triangles and two BO_4 tetrahedron. But the relationship between Mg and the B–O group occurs in inderite in a way quite different from kurnakovite. The borate group can be considered as less regular in inderite than in kurnakovite if the ideal regular group is defined as one in which the ring plane is a plane of symmetry [2]. Recently, we discovered a new form of $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$ when investigating the phase transformation of $2\text{MgO}\cdot 2\text{B}_2\text{O}_3\cdot \text{MgCl}_2\cdot 14\text{H}_2\text{O}$ in boric acid aqueous solution at 0°C . Its structure has been studied using XRD, FT-IR, and Raman spectra as well as TG.

Thermodynamic properties play very important roles in scientific research and industrial applications. Li et al. [3]

reported the standard molar enthalpy of formation of eight hydrated magnesium borates. This paper reports the synthesis and the standard molar enthalpy of formation of a new form of $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$.

2. Experimental

2.1. Synthesis of a new form of $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$

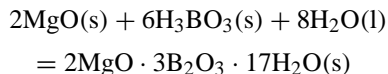
The new form of $2\text{MgO}\cdot 3\text{B}_2\text{O}_3\cdot 17\text{H}_2\text{O}$ was synthesized by the method of phase transformation of double salt as follows: 1.86 g of $2\text{MgO}\cdot 2\text{B}_2\text{O}_3\cdot \text{MgCl}_2\cdot 14\text{H}_2\text{O}$ (synthesized by modification of the literature method [4]), 0.85 g of H_3BO_3 (mass fraction $\geq 99.8\%$), and 40 ml of H_2O were transferred to a flask with a stirrer, and set in a constant temperature water bath at 0°C . After the reaction mixture was stirred for 3 days, the solid in solution was separated, washed thoroughly with alcohol and then ether. Finally, the obtained solid was dried in a vacuum dryer to a constant mass at room temperature, and was characterized by X-ray powder diffraction (recorded on a Rigaku D/MAX-IIIC), FT-IR spectroscopy (recorded over the $400\text{--}4000\text{ cm}^{-1}$ region on a Bruker Equinox 55 spectrometer with KBr pellets at room temperature), Raman spectroscopy (recorded over the $200\text{--}1000\text{ cm}^{-1}$ region on a Nicolet Omega Dispersive Ramanmeter), and TG (determined on a METZSCH-Geratebau GmbH STA449C Thermal Analyzer at a heating rate of

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10 °C min⁻¹ in flowing N₂). The chemical composition of the sample was determined by EDTA titration for Mg²⁺, by NaOH standard solution in the presence of mannitol for B₂O₃, and by difference for H₂O.

2.2. Method of calorimetric experiment

The new form of 2MgO·3B₂O₃·17H₂O can be regarded as the product of the following reaction:



The standard molar enthalpy of formation of a new form of 2MgO·3B₂O₃·17H₂O could be obtained by solution calorimetry in combination with the standard molar enthalpies of formation of MgO(s), H₃BO₃(s), and H₂O(l). The H₃BO₃ and the synthetic sample were dissolved in approximately 1 mol dm⁻³ HCl(aq), respectively, and then the calculated amount of MgO was dissolved in aqueous (hydrochloric acid + boric acid) which consisted of approximately 1 mol dm⁻³ HCl(aq) and the calculated amount of H₃BO₃. The HCl solvent was prepared from analytical grade hydrochloric acid and deionized water, and its concentration was determined by titration with standard sodium carbonate.

A RD496-III heat conduction microcalorimeter (Southwest Institute of Electron Engineering, China) was used and has been described in detail previously [5]. The temperature of the calorimetric experiment was 298.15 K. Additional double-layer glass tubes were put in the 15 ml stainless steel sample cell and reference cell of the calorimeter. This was done to prevent corrosion of the stainless steel sample and reference cell by HCl(aq). The lining in the double-layer glass tube containing HCl(aq) was broken by a rod after thermal equilibration for at least 2 h. The HCl(aq) was mixed with solid sample in the outer glass tube, then the thermal effect was recorded automatically on a computer. Total time required for the complete reaction was about 0.5 h. There were no solid residues observed after the reactions in each calorimetric experiment.

To check the performance of RD496-III heat conduction microcalorimeter, calorimetric measurements on the enthalpy of solution of KCl (spectral purity) in deionized water were made. The experimental mean value (17.23 ± 0.04) kJ mol⁻¹ of $\Delta_{\text{sol}}H_m$ is in excellent agreement with that of (17.241 ± 0.018) kJ mol⁻¹ reported in the literature [6]. This result shows that the device for measuring the enthalpy of solution used in this work is reliable.

3. Results and discussion

3.1. Characterization of the synthetic sample

Chemical analysis results of synthetic sample: MgO, 13.50%; B₂O₃, 35.20%; H₂O, 51.30%; mole ratio of MgO:B₂O₃:H₂O = 2.00:3.02:17.01.

XRD data of synthetic sample, *d* (Å), (*I*/*I*₀): 9.605(100), 7.076(20), 6.573(12), 6.412(25), 6.138(68), 5.175(12), 5.024(24), 4.706(12), 4.530(41), 4.304(30), 3.531(17), 3.448(15), 3.356(16), 3.266(20), 3.225(29), 3.123(35), 2.833(39), 2.682(19), 2.549(15), 2.429(17), 2.264(15), 2.047(16), and 1.881(14). It can be seen that the shape and data of XRD spectra of synthetic sample are different from those of 2MgO·3B₂O₃·17H₂O reported in the literature [1], which indicates that the synthetic sample is a new compound.

The IR and Raman spectra of synthetic sample exhibited the following absorptions and they were assigned referring to literature [7]. The band at 3336 cm⁻¹ is the stretching of O–H. The band at 1655 cm⁻¹ is assigned to the H–O–H bending mode, which shows the compound containing the crystal water. The bands at 1398 and 1356 cm⁻¹ might be the asymmetric stretching of B(3)–O. The bands at 1139, 1053, 1001 cm⁻¹ and 889, 806, and 748 cm⁻¹ (Raman) are assigned as the asymmetric and symmetric stretching of B(4)–O, respectively. The band at 667 cm⁻¹ in IR and 631 cm⁻¹ in Raman are assigned as the characteristic peak of tetraborate anion, which shows that the synthetic sample contains the [B₃O₃(OH)₅]²⁻. The bands at 508 cm⁻¹ in IR and 490, 409, 325 cm⁻¹ in Raman are the bending modes of B(4)–O.

TG curve (Fig. 1) indicates that the total mass loss is 51.51% from 50 to 600 °C, which corresponds to the loss of 17 water molecules and can be compared with calculated value of 51.39%. On the DSC curve (Fig. 1), there are two peaks: one endothermic peak ($\Delta_r H_m = 555.39$ kJ mol⁻¹) appeared at 89 °C corresponds to the loss of 17 water molecules and formed amorphous 2MgO·3B₂O₃; the other greater exothermic peak ($\Delta_r H_m = -51.46$ kJ mol⁻¹) appeared at 760 °C corresponds to a recrystallization of 2MgO·3B₂O₃.

Therefore, the synthetic sample is a new form of 2MgO·3B₂O₃·17H₂O reported in the literature [1]. In the following, our form of 2MgO·3B₂O₃·17H₂O will be named β-2MgO·3B₂O₃·17H₂O and Li et al. [1] α-2MgO·3B₂O₃·17H₂O. Although their structural formula can be both written as Mg[B₃O₃(OH)₅]₃·6H₂O, the regular of [B₃O₃(OH)₅]²⁻ groups in their structure may be different, which is similar to the case in inderite and kurnakovite. No impurity lines were observed, and the synthetic sample is suitable for the calorimetric experiments.

3.2. Results of calorimetric experiment

The results of the calorimetric measurements are given in Table 1, in which *m* is the mass of sample, $\Delta_{\text{sol}}H_m$ is the molar enthalpy of solution of solute, and the uncertainty is estimated as twice the standard deviation of the mean. Table 2 gives the thermochemical cycle for the derivation of the standard molar enthalpy of formation of the β-2MgO·3B₂O₃·17H₂O. The molar enthalpy of solution of H₃BO₃(s) of (21.83 ± 0.08) kJ mol⁻¹ in approxi-

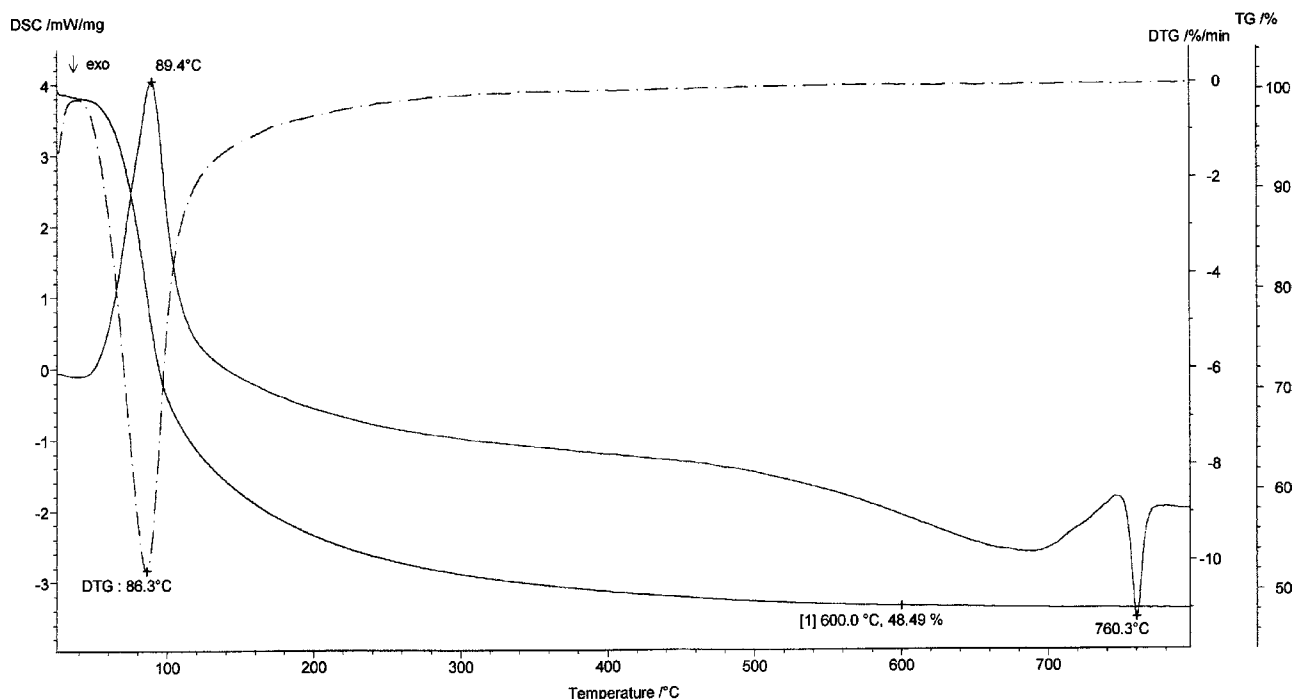


Fig. 1. Simultaneous TG-DSC curves of synthetic sample.

Table 1

The molar enthalpies of solution of β -2MgO·3B₂O₃·17H₂O in approximately 1 mol dm⁻³ HCl at 298.15 K^a

No.	<i>m</i> (mg)	$\Delta_{\text{sol}}H_{\text{m}}$ (kJ mol ⁻¹)
1	4.94	36.18
2	4.93	36.09
3	5.03	36.18
4	5.04	36.14
5	4.98	36.26
Mean		36.17 ± 0.06 ^b

^a In each experiment, 2.00 cm³ of HCl(aq) was used.

^b Uncertainty is estimated as twice the standard deviation of the mean.

mately 1 mol dm⁻³ HCl(aq), and of MgO(s) of $-(146.20 \pm 0.36)$ kJ mol⁻¹ in the mixture of HCl and H₃BO₃ were taken from literature [3]. The standard molar enthalpies of formation of H₂O(l), MgO(s), and H₃BO₃(s) were taken from the CODATA Key Values [8], namely $-(285.830 \pm 0.040)$, $-(601.60 \pm 0.30)$, and $-(1094.8 \pm 0.8)$ kJ mol⁻¹, respectively. The enthalpy of dilution HCl(aq) was calculated from

the NBS tables [9]. From these data, the standard molar enthalpy of formation of β -2MgO·3B₂O₃·17H₂O was calculated to be $-(10256.39 \pm 4.93)$ kJ mol⁻¹. This result is different from that of 2MgO·3B₂O₃·17H₂O reported in the literature [3], which also shows that the synthetic sample is a new form of 2MgO·3B₂O₃·17H₂O reported in the literature [1]. The enthalpy of formation of β -2MgO·3B₂O₃·17H₂O can also be estimated by a group contribution method [10] as the sum of the contributions of Mg²⁺(aq), [B₃O₃(OH)₅]²⁻(aq) and of structural water. The standard molar enthalpy of formation is, using this scheme, -10244.46 kJ mol⁻¹. The calculated value is close to the experimental result. The relative error is 0.12%.

We also used a group contribution method to calculate $\Delta_{\text{f}}G_{\text{m}}^{\circ}$ of the β -2MgO·3B₂O₃·17H₂O to be -8974.14 kJ mol⁻¹. Combining its $\Delta_{\text{f}}H_{\text{m}}^{\circ}$, the standard molar entropy of formation of the β -2MgO·3B₂O₃·17H₂O has been calculated at -4300.69 J mol⁻¹ K⁻¹ according to following equation:

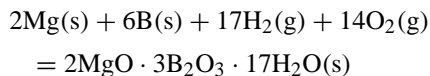
$$\Delta_{\text{f}}S_{\text{m}}^{\circ} = \frac{\Delta_{\text{f}}H_{\text{m}}^{\circ} - \Delta_{\text{f}}G_{\text{m}}^{\circ}}{T}$$

Table 2

Thermochemical cycle and results for the derivation of $\Delta_{\text{f}}H_{\text{m}}^{\circ}$ (β -2MgO·3B₂O₃·17H₂O, 298.15 K)

No.	Reaction	$\Delta_{\text{r}}H_{\text{m}}$ (kJ mol ⁻¹)
1	6H ₃ BO ₃ (s) + 238.276(HCl·54.561H ₂ O) = 6H ₃ BO ₃ (aq) + 238.276(HCl·54.561H ₂ O)	130.98 ± 0.48
2	2MgO(s) + 6H ₃ BO ₃ (aq) + 238.276(HCl·54.561H ₂ O) = 2MgCl ₂ (aq) + 6H ₃ BO ₃ (aq) + 234.276(HCl·55.505H ₂ O)	-292.40 ± 0.72
3	2MgCl ₂ (aq) + 6H ₃ BO ₃ (aq) + 234.276(HCl·55.505H ₂ O) = 2MgO·3B ₂ O ₃ ·17H ₂ O(s) + 238.276(HCl·54.527H ₂ O)	-36.17 ± 0.06
4	238.276(HCl·54.527H ₂ O) + 8H ₂ O = 238.276(HCl·54.561H ₂ O)	-0.16 ± 0.01
5	2MgO(s) + 6H ₃ BO ₃ (s) + 8H ₂ O(l) = 2MgO·3B ₂ O ₃ ·17H ₂ O(s)	-197.75 ± 0.87

Finally, the standard molar entropy of the β -2MgO·3B₂O₃·17H₂O was calculated to be 890.36 J mol⁻¹ K⁻¹ according to following reaction:



The standard molar entropies of the elements were taken from CODATA Key Values to be 32.67, 5.90, 130.571, and 205.043 J mol⁻¹ K⁻¹ for Mg(s), B(s), H₂(g), and O₂(g), respectively.

It can be seen from the results of literature [3] that the $\Delta_f H_m^\circ$ of inderite is bigger than that of kurnakovite, which is consistent with the fact that the inderite is more stable than kurnakovite. In present paper, the determined $\Delta_f H_m^\circ$ of β -2MgO·3B₂O₃·17H₂O is less than that of α -2MgO·3B₂O₃·17H₂O reported in the literature [3], the difference of which is mainly due to the difference of regular of [B₃O₃(OH)₅]²⁻ in their structure as if the case of the former pair. This result shows that the β -2MgO·3B₂O₃·17H₂O is less stable than α -2MgO·3B₂O₃·17H₂O.

Acknowledgements

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