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Synthesis of chloropinnoite and phase interaction with water at high temperatures[1]

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Abstract

A new magnesium-borate double salt which was nominated as chloropinnoite was synthesized and the phase interaction with water at 478±5 K and 553±5 K studied. The results suggest that certain pure magnesium-borates can be synthesized from chloropinnoite–water system under different conditions, and the physico-chemical data of these borates can be obtained.

1. Introduction

The brine of Dachadam Salt Lake, which belongs to borate salt lake of the $MgSO_4$-subtype, mainly contains chlorides, sulphates, and borates of sodium, potassium, magnesium and lithium. It has been of geological, mineralogical, chemical and commercial interest since its discovery in 1957 [1]. When the brine was evaporated and concentrated in a solar pond, the boron concentration increased up to 2.5% B_2O_3. At the same time, from $MgSO_4$-saturated brine in which mirabilite has been dissolved beforehand, we obtained the eutectic concentrated borate brine, containing 7.5% MgB_4O, 20.08% $MgCl_2$, 5.78% $MgSO_4$. 2.08% KCl and 0.5% NaCl [1]. Gao Shiyang [2] obtained two kinds of borates from the concentrated brine, one of them being $MgO{\cdot}3B_2O_3{\cdot}7H_2O$ and the other – a new borate double salt which was given the nomenclature chloropinnoite, $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$. It is similar to the "eutectic borate", which is written as $XMgO{\cdot}YB_2O_4{\cdot}MgCl_2{\cdot}ZH_2O$ [3], obtained by M.G. Valyashko from Inder Salt Lake brine. The new borate double salt is a small pillared crystal, when seen under the microscope. These authors [3] recorded the X-ray powder diffraction spectra, IR spectra and thermal analysis of the borate, and observed double exothermal peaks. These peaks were similar to those in the DTA curve of pinnoite ($MgO{\cdot}B_2O_3{\cdot}H_2O$). Therefore, the borate was named as chloropinnoite [2]. In this paper, a new synthetic method for preparing chloropinnoite and its phase interaction with water at high temperatures (478±5 K, 553±5 K) have been reported.

2. The synthesis and identification of chloropinnoite

The weighed amounts of $MgCl_2{\cdot}6H_2O$ (A.R.), H_3BO_3 (A.R.) and MgO (obtained by the decomposi-

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Table 1
The chemical analysis results of synthesized $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$

Run	Composition (wt%)				Molar ratio			
	B_2O_3	MgO	$MgCl_2$	H_2O	B_2O_3	MgO	$MgCl_2$	H_2O
1	24.57	14.32	16.82	44.29	2.00	2.01	1.00	13.92
2	24.65	14.30	16.79	44.26	2.01	2.01	1.00	13.94
3	24.09	14.24	16.78	44.89	1.96	2.00	1.00	14.15

tion of $Mg(OH)_2{\cdot}4MgCO_3{\cdot}6H_2O$ at 873 K for ca. 3 h) were dissolved in double distilled water (stirring and heating until all the solids disappeared). The solution was filtered and the obtained clear solution (composition – 2.00% H_3BO_3, 0.65% MgO, 32.00% $MgCl_2$ and 65.35% H_2O) was put in a crystallizer which was thermostated at 313 K, and some seeds of chloropinnoite were added. When a lot of crystals crystallized out, the solid was separated from the solution and washed with absolute ethyl alcohol until there was almost no Cl^- in the mother liquor. Thereafter, the solid was washed again with ether. The obtained solid was dried in a vacuum dryer to a constant weight at room temperature. The results of chemical analysis (Table 1), X-ray powder diffraction (Fig. 1). IR spectra (Fig. 2) and thermal analysis (Fig. 3) showed that all the synthesized $2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$ samples were pure compounds and suitable for the following experiments.

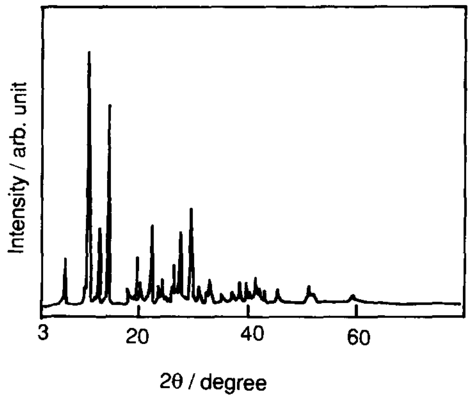

Fig. 1. The X-ray powder diffraction result of synthesized chloropinnoite.

3. Experimental

3.1. The phase interaction of chloropinnoite with water

The two-chamber pressure vessel for hydrothermal solubility determination (Fig. 4) [4] was used for investigation of chloropinnoite interaction with water at 478 K, 553 K and vapour pressures. The weighed quantities of chloropinnoite and distilled water were placed in chamber 1. The vessel was kept closed and placed in a rocking furnace. For each equilibrium, the mixture was stirred by rocking and the temperature maintained during 5–8 h, with an accuracy of ±5 K.

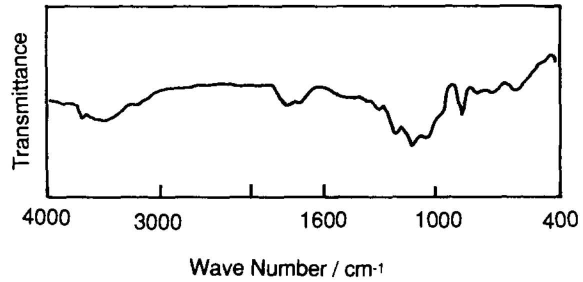

Fig. 2. The IR spectrum of synthesized chloropinnoite.

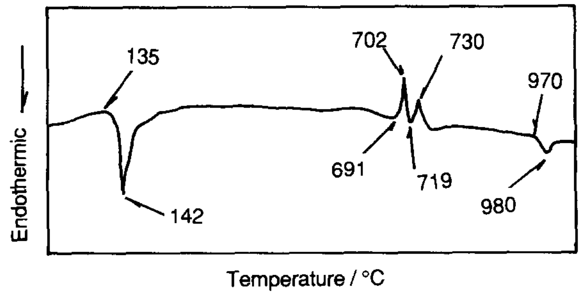

Fig. 3. The thermal analytic curve of synthesized chloropinnoite.

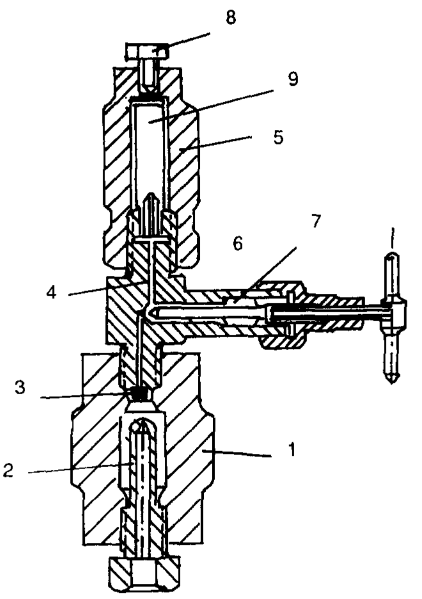

Fig. 4. Two-chamber pressure vessel for solubility determination: 1 – pressure vessel where the charge is placed; 2 – thermocouple well; 3 – filter made of pressed, fine silver wire; 4 – channel between two chambers; 5 – sampler; 6 – needle valve; 7 – valve packing; (Teflon, asbestos with graphate); 8 – screw; and 9 – metallic cup for sampling.

Then the vessel was turned over, the valve opened, a liquid phase was pressed through the filter 3 into an empty sampler 5, and the value closed again. After cooling down to room temperature, the metallic cup 9, with a sample, was removed from the sampler and weighed for determination of sample quantity. The composition of the solution was determined by EDTA titration for Mg^{2+}, by $Ba(OH)_2$ solution for B_2O_3 and by $AgNO_3$ solution for Cl^-. At the same time, the separated solid phase taken from the chamber 1 was identified by X-ray powder diffraction, IR spectrum, and chemical analysis, respectively.

4. Results

The chemical compositions of the equilibrium solid and liquid phases at 478±5 K and 553±5 K are listed in Table 2. A part of the X-ray powder diffraction and IR spectra of the solid phases are shown in Figs. 5 and 6. The X-ray diffraction and IR data are listed in Tables 3 and 4. From a comparison with the literature results [4,5], we could conclude that the equilibrium solid phase was asharite ($2MgO{\cdot}B_2O{\cdot}(1\text{–}2)H_2O$) (asharite which formed at high temperature would not change to other compound(s) and it could not be formed at low temperatures).

4.1. *The phase interaction mechanism of chloropinnoite with water*

Chloropinnoite ($2MgO{\cdot}2B_2O_3{\cdot}MgCl_2{\cdot}14H_2O$) might be regarded as a carnillate-like double salt and the formula could be written as

Table 2
Chemical composition of liquid and solid phases

Run	Charged mixture					Equilibrium liquid phase				Solid phase	
	T(K)	B_2O_3 wt.%	MgO wt.%	$MgCl_2$ wt.%	H_2O wt.%	B_2O_3 wt.%	MgO wt.%	$MgCl_2$ wt.%	H_2O wt.%	MgO : B_2O_3 mole ratio	
1	478±5	0.43	0.23	0.29	99.05	0.25	0.02	0.29	99.44	2.005 [a]	No [b]
2	478±5	0.93	0.49	0.62	97.96	0.55	—	0.62	98.83	2.200	2.025
3	478±5	1.20	0.63	0.80	97.37	0.67	—	0.80	98.53	2.027	2.007
4	478±5	1.63	0.85	1.08	96.44	0.91	—	1.08	98.01	2.047	2.054
5	478±5	2.32	1.21	1.55	94.92	1.26	—	1.55	97.19	1.985	2.078
6	553±5	1.18	0.61	0.78	97.43	0.64	—	0.78	98.58	1.971	2.100
7	553±5	1.74	0.91	1.16	96.18	0.96	—	1.16	97.88	2.000	1.995
8	553±5	2.21	1.16	1.48	95.15	1.20	—	1.48	97.32	1.985	2.001
9	553±5	2.25	1.18	1.50	95.07	1.34	0.04	1.50	97.12	2.150	2.098

[a] Calculated as a difference between the compositions of initial mixture and equilibrium liquid phase from solution.[b] Determined from residue solid phase by chemical analysis.

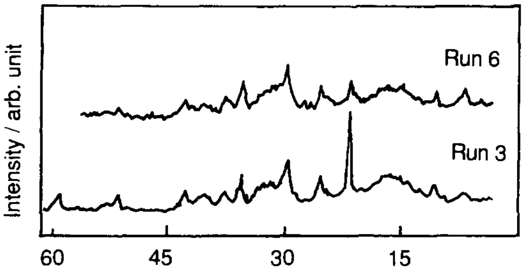

Fig. 5. The X-ray powder diffraction of some residual solids.

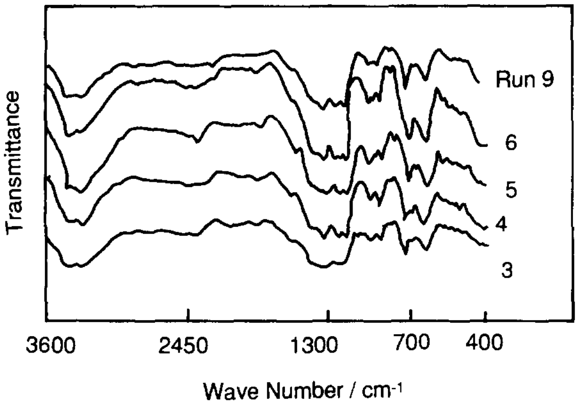

Fig. 6. The IR spectra of some residual solids.

$2[MgB_2O(OH)_6{\cdot}H_2O{\cdot}H_2O][Mg(6H_2O)Cl_2]$. While it dissolved in water, a complicated multi-step process is possible. The dissolution reaction mechanism may be written as follows:

The first step is

$$\begin{aligned}&2MgO\cdot 2B_2O_3\cdot MgCl_2\cdot 14H_2O + nH_2O\\&\quad = 2[MgB_2O(OH)_6\cdot H_2O] + [Mg(6H_2O)Cl_2]\\&\quad + nH_2O = 2[MgB_2(OH)_6\cdot H_2O] + Mg^{2+}\\&\quad + 2Cl + (n+6)H_2O\end{aligned}$$

as the constituent $[Mg(6H_2O)Cl_2]$ is a highly soluble component and it is easy to dissolve in water. The other constituent $MgB_2O(OH)_6{\cdot}H_2O$ may be an insoluble component and it remains as an amorphous intermediate product at room temperature [6].

The second step, the dissociation and transformation of the intermediate product may be given as:

$$2[B_2O(OH)_6]^{2-}[B_4O_5(OH)_4]^{2-} + 3H_2O + 2OH'$$

$$3[B_4O_5(OH)_4]^{2-} + 2H_2O4[B_3O_3(OH)_4] + 2OH'$$

$$2[B_3O_3(OH)_4]' + 2OH'[B_6O_7(OH)_8]^{4-} + H_2O$$

The polyborate anion $(B_6O\text{-}(OH)_3]^{4-}$ in aqueous solution with Mg^{2+} at 283–323 K forms inderite.

$$\begin{aligned}&[B_6O_7(OH)_8]^{4-} + 2eMg^{2+}\\&\quad + 11H_2OMg_2[B_6O_7(OH)_8]\cdot 11H_2O\end{aligned}$$

the polyborate anion $[B_2O(OH)_6]^{2-}$ combined Mg^{2+} directly and formed pinnoite at ca. 333 K [6].

$$[B_2O(OH)_5]^{2-} + Mg^{2+}Mg[B_2O(OH)_6]$$

when the temperature is at 473–553 K, a phase interaction might be carried out in the high temperature solution, two $[MgB_2O(OH)_6{\cdot}H_2O]$ molecules were

Table 3
X-ray powder diffraction results of some solid phases

No.	Run 3			No.	Run 6		
	2θ°	θ°	d/Å		2θ°	θ°	d/Å
1	14.0	7.0	6.3255	1	14.0	7.0	6.3255
2	17.2	8.6	5.1552	2	17.3	8.65	5.1257
3	22.3	11.15	3.9864	3	23.0	11.5	3.8667
4	26.8	13.4	3.3264	4	26.8	13.4	3.3264
5	30.0	15.0	2.9785	5	30.0	15.0	2.9785
6	33.6	16.8	2.6671	6	34.0	17.0	2.6367
7	39.0	19.5	2.3094	7	39.0	19.5	2.3094
8	40.8	20.4	2.2116	8	40.8	20.4	2.2116
9	46.2	21.6	2.0941	9	43.5	21.75	2.0804
10	45.5	26.5	1.7277	10	45.7	22.85	1.9852
11	53.0	26.5	1.7277	11	53.0	26.5	1.7277
12	59.5	29.75	1.5535	—	—	—	—

Table 4
The IR frequencies (in cm^{-1}) of some solid phases

Run 3	Run 4	Run 5	Run 6	Run 9	Chloropinnoite
405m	407m	408m	407m	430w	401w
495m	495m	495m	490m	490m	420w
540m	540m	540m	540m	540m	515w
565m	570m	570m	568m	568m	625b,w
630s	630vs	630s	629s	630s	725b,w
650w	685w	685w	681m	682w	810s
710vs	710vs	710s	710vs	710vs	952m
—	—	830w	780w	830w	1045m
845m	840m	845m	845m	845m	1055m
930s	930s	935m	930s	930s	1135s
985m	985m	990w	985m	985m	1250m
1020m	1021m	1020m	1020m	1020m	1300w
1085w	1090w	1090w	—	—	1430w
1220m	1220m	1220m	1220m	1220m	1675m
1290m	12890m	1290m	1287m	1290m	1700w
1380s	1380s	1380s	1380s	1380m	2950w
1480w	1480w	1500w	1495m	1495w	3025w
1650w	1640w	1680w	1650m	1650m	3420s
	1730w	1855w	1815w	1950w	3465s
2390m	2380m		2540w	2530b,m	3530w
3430b,m	3455b	3430b,m	3440b,m	3430b,m	3475w
3565m	3560m	3560m	3560b,m	3560b,m	—

"hydrothermally calcined" and formed a asharite molecule to crystallize out, at the same time a molecule of B_2O_3 was given out and entered into solution as H_3BO_3:

$$2[MgB_2O(OH)_6] \cdot H_2O2MgO \cdot B_2O_3 \cdot H_2O + B_2O_3 + H_2O$$

$$B_2O_3 + H_2OH_3BO_3$$

4.2. *The possibility to synthesise a series of borates from chloropinnoite*

As already mentioned, we have obtained hydrated magnesium borates from the phase interaction of chloropinnoite with water under different experimental conditions: inderite ($Mg_2[B_6O_7(OH)_6 \cdot 11H_2O$ (the mole ratio MgO/B_2O_3 is 2 : 3) at 283–323 K; pinnoite ($Mg[B_2(OH)_6]$, $MgO/B_2O_3=1:1$) at ca. 333 K, asharite ($Mg_2B_2O_4 \cdot (1\text{–}2)H_2O$, $MgO/B_2O_3=2:1$) at 478±5–553±5 K. It is obvious that the $MgO : B_2O_3$ molar ratio of the phase interaction products increases as the temperature increases. Recently, Ishihara et al. [3] studied the rapid exchanges of B^* between $B(OH)_4$ with ^{11}B NMR and suggested that there might exist a diborate anion as an intermediate product during this process. The intermediate product could be transformed into different borates. Comparing with our results, it is reasonable to think that some magnesium borates with different $MgO : B_2O_3$ molar ratios would be synthesized by the phase interaction of chloropinnoite with water in a different temperature range.

5. Conclusions

1. $MgCl_2$ is leaching from chloropinnoite in hydrothermal conditions.
2. The asharite arises as a main equilibrium solid phase in the interaction of chloropinnoite with water at (478–553)±5 K and vapor pressures.
3. It is possible to synthesize different magnesium borates by the phase interaction of chloropinnoite with water under different conditions.

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