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采用稀释成盐法从富硼浓缩盐卤中合成的镁硼酸盐化合物及其结构与性质

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摘要:通过稀释成盐法在富硼浓缩盐卤体系 Na-K-Mg-Cl-SO_4 中合成了一种新的六硼酸镁 $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ 化合物。根据 X射线粉末衍射数据对其晶体结构进行了精修,并采用红外及拉曼光谱法对其结构进行了表征,分析了其光谱及结构特征。结果表明,该化合物由 1 个 Mg 原子、1 个 $B_6O_7(OH)_6$ 基团和 5 个 H_2O 分子构成,Mg 原子以六配位形式与氧结合形成畸变 MgO_6 八面体构型;热重分析表明,高温分解过程该化合物脱水转化为四硼酸镁 MgB_4O_7;通过紫外可见漫反射法求得其禁带宽度为 4.44 eV。

关键词:镁硼酸盐;含硼盐卤;稀释成盐法;结构;热稳定性

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Synthesis, Structure and Properties of a Magnesium Borate in Concentrated Boron-Bearing Salt Lake Brine by Dilution Method

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Abstract: A new magnesium borate mineral, $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ was synthesized via dilution method from boron-bearing Na-K-Mg-Cl-SO_4 salt lakes. The crystal structure of the new phase was solved and refined using X-ray powder diffraction data and characterized with FTIR and Raman. Its asymmetric unit consists of one Mg atom, one $B_6O_7(OH)_6$ cluster and five H_2O molecules. The Mg atom is 6-coordinated with six O atoms to form a MgO_6 octahedron. Thermal gravimetry (TG/DSC) was used to investigate the thermal behavior of the new compound. During the high temperature decomposition process the dehydrated product MgB_4O_7 formed. The optical absorption characteristic of this new mineral was investigated by UV-Vis spectrometer and its energy gap E_g is about 4.44 eV.

Keywords: magnesium borate; boron-bearing salt lake; dilution method; structure; thermal behavior

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0 Introduction

Boron and its compounds are important inorganic salt products. Especially materials enriched in boron-10 are widely used in nuclear power, military equipment, and pharmaceuticals, etc, based on the property that boron-10 can absorb thermal neutrons. For example, the boric acid enriched in boron-10 used as neutron absorber in nuclear power can effectively ensure the nuclear reactor′s safe operation[1]. Furthermore, boron minerals, owing to their high heat resistance, light weight, fire retardency, nonlinear optics and anti-wear properties, can be widely applied in ceramics, metallurgy, building materials and electronic areas[2-5]. In recent years, with the increasing demand of boron products and the difficulty exploitation of low grade boron ores, boron exploitation from salt lake brine has become an important means to produce boron products[6].

Lake Da Qaidam is one of the magnesium sulfate subtype salt lakes found on Qinghai Tibet Plateau in western China. The brine of which is abundant in sodium, potassium, magnesium, lithium and boron mineral resources. The main composition of the brine is Na-K-Mg-Cl-SO_4. And the crystallization path about summer brine during evaporation was[7]:

halite → halite +epsomite → halite +epsomite + hexahydrite +sylvite → halite +hexahydrite +sylvite + carnallite →halite+hexahydrite+carnallite+bischofite.

When the brine evaporation path went into bischofite crystallization, the brine is rich in boron and lithium resources and can be used as raw material for the production of boron and lithium products. Gao and Li have investigated the chemical behavior of the borate during brine evaporation[8]. They found that the borate in this brine, in general, does not crystallize out but accumulates in the highly concentrated brine, in the form of polyborate anions of "tetraborate" by statistics. The supersolubility of boron enriched in the brine can reach up to 5.82% in B_2O_3[9]. However, the fact will be exactly the opposite when diluting the boron-bearing highly concentrated brine with some water. Kinds of Mg-borate salts would participate after diluting the brine for a period of time and the deposit salts changed with the dilution ratio of brine[10]. This phenomenon is quite different to crystallization by evaporation. Gao called it as "crystallization by dilution". The salts precipitated from diluted brine contain magnesium borate hydrate ($MgO(B_2O_3)_3\cdot 6H_2O$), macallisterite ($Mg_2[B_6O_7(OH)_6]_2\cdot 9H_2O$), admontite ($MgO(B_2O_3)_3\cdot 7H_2O$), hungchsaoite ($Mg(H_2O)_5B_4O_5(OH)_4\cdot 2H_2O$), kurnakovite ($MgB_3O_3(OH)_5(H_2O)_4\cdot H_2O$) and inderite ($MgB_3O_3(OH)_5(H_2O)_4\cdot H_2O$). The above results of "crystallization by dilution" indicate a possible economic extraction of boron resources from brine. Thus, we just call it as dilution method compared with traditional methods of acid precipitation and solvent extraction. During the dilution crystallization process, we found a new Mg-borate compound of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ from the highly concentrated brine. The present study aims to report the synthesis, structural characterization, optical and thermal properties of this new compound.

1 Experimental

1.1 Materials and measurements

Mirabilite ores ($Na_2SO_4\cdot 10H_2O$) were used to remove parts of Mg^{2+} ion from brine for further evaporation purpose. The Raman spectra were recorded using a Raman spectrometer (ALMEGA-TM, Therm Nicolet, American) with the linearly polarized 532.0 nm line of a diode laser. The spectra were taken from 300 to 1 500 cm^{-1} since the characteristic peaks of borate compounds were given in the range of 1 500~500 cm^{-1}[11]. The FTIR spectrum was obtained on a Fourier transform IR spectrometer (NEXUS, Therm Nicolet, American) with KBr pellet in the range of 400~4 000 cm^{-1} at room temperature. The DSC and TG measurements were performed simultaneously using a scanning calorimeter (NETZSCH STA, 449F3) heating from 30 to 1 200 ℃ in nitrogen atmosphere with a constant heating rate of 5 ℃·min^{-1}. The Mg and B elements of the product was investigated by the inductive coupling plasma (ICP) spectrometer (Thermo, 6500) and the O element was measured by an Oxford series X-ray energy dispersion spectrometer

(EDS). The UV/Vis diffuse spectrum for $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ was recorded with a Agilent Cary 5000 spectrophotometer in the range from 200 to 800 nm at room temperature.

1.2 Preparation of the concentrated boron-bearing brine

When the brine evaporation path went into bischofite crystallization, the boron content in brine is about 1.3% in B_2O_3 which is too low to extract boron from brine by dilution method. Further evaporation is needed to concentrate the boron element. However, since the brine with saturated bischofite is extremely high-saline, viscous and hygroscopic and tends to absorb humidity from the air rather than drying. This brine can hardly be further concentrated by natural evaporation. In this study, according to the following reaction:

$$Na_2SO_4\cdot 10H_2O(s)+MgCl_2(aq) \rightleftharpoons MgSO_4(aq)+2NaCl(s)+10H_2O(l)$$

some mirabilite ores were added into the brine at 25 ℃ to react with the magnesium chloride generating magnesium sulfate and sodium chloride. Then the brine saturated with epsomite and halite can be easily further evaporated at room temperature. Therefore, the concentrated boron-bearing brine can be obtained by evaporation.

1.3 Synthesis of the magnesium borate of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$

The concentrated boron-bearing brine with boron content above 4% B_2O_3 was used as materials to synthesize the new compound of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$. First, an amount of the concentrated brine was diluted with some water, the mass ratio of brine and water was 1∶0.25. The solution was stirred for about 20 min each day at room temperature until the participation of solid phase, then aged and filtrated after a week. The sediment was washed by water and absolute alcohol, respectively, and dried in a vacuum drying oven for 24 h. The chemical composition of the obtained product was analyzed by titration.

1.4 X-ray powder diffraction crystallography

A laboratory powder diffractometer (X′Pert PRO, 2006 PANalytical, Cu $K\alpha_1$), with a tube voltage and current of 40 kV and 30 mA, was used to confirm the $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ phase purity. The powder pattern was measured in the scanning range from 3.502 0° to 109.998 0°, 2θ with a scan step of 0.002° and at a fixed counting time of 16 s per step.

Owing to the difficulty to grow crystals suitable for single-crystal structure determination, the crystal structure was solved and refined using conventional X-ray powder diffraction techniques. The TOPAS 4.2 program suite[12] was used for indexing, obtaining structure solution, and refinement of the crystal structure model. The iterative least squares algorithm (LSI)[13] was employed to index the pattern, and resulted in a primitive monoclinic lattice. The unit cell and profile parameters were refined by a Pawley fit[14] using the fundamental parameters approach[15]. The background was modelled by a Chebychev polynamial of 10th order.

2 Results and discussion

2.1 Evaporation crystallization path

The brine evolution during evaporation was represented graphically on the metastable phase diagram of Na^+, K^+, Mg^{2+}/Cl, SO_4^{2-}//H_2O at 25 ℃[16] (Fig.1). Its composition was listed in Table 1. In Fig. 1, DL_0 was the residue bittern of Da Qaidam salt lake during evaporation and its system was located in the bischofite phase. After removing parts of Mg^{2+} ion by adding some mirabilite ores, the brine system "DL_1" gone into the epsomite region and is easy to concentrate by evaporation. When the crystallization path

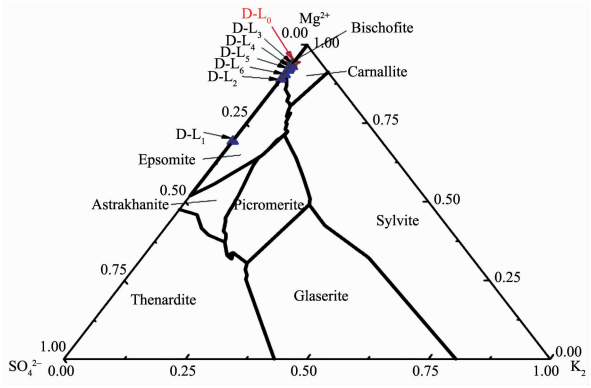

Fig.1 Crystallization path of brine DL_1 at metastable diagram of Na^+, K^+, Mg^{2+}/Cl, SO_4^{2-}//H_2O at 25 ℃

Table 1 Evolution of major ion concentrations during evaporation at ambient temperature

Brine	Concentration / %						
	Na^+	Mg^{2+}	K^+	B_2O_3	Cl^-	SO_4^{2-}	Li^+
DL_0	0.107±0.003	8.863±0.086	0.048±0.001	1.284±0.009	24.472±0.160	2.268±0.004	0.144 0±0.003
DL_1	2.577±0.125	5.515±0.031	0.037±0.001	0.970±0.005	13.020±0.498	9.638±0.017	0.104 0±0.001
DL_2	0.122±0.006	8.022±0.051	0.084±0.001	2.187±0.012	20.797±0.861	3.832±0.007	0.209 8±0.002
DL_3	−0.072±0.02	8.782±0.054	0.059±0.001	2.825±0.020	23.665±0.158	2.474±0.004	0.267 6±0.006
DL_4	0.424±0.017	8.869±0.060	0.063±0.001	3.244±0.021	23.592±0.181	2.806±0.005	0.142 8±0.005
DL_5	−0.041±0.001	8.773±0.059	0.063±0.001	4.352±0.039	22.671±0.145	3.018±0.005	0.298 4±0.004
DL_6	0.055±0.003	8.636±0.055	0.087±0.001	5.163±0.028	21.96 0±1.023	3.538±0.006	0.360 9±0.003

evolved from epsomite (DL_1) to bischofite (DL_3), the boron content in brine was concentrated to about 3% in B_2O_3 (Table 1). This brine can be used to extract boron by dilution method. But, for the synthesis of the new compound, it will be further evaporated until the boron content is above 4% B_2O_3. Therefore, the concentrated boron-bearing brine DL_5 or DL_6 obtained by evaporation were used as materials for the synthesis of the new compound.

2.2 XRD pattern and crystal structure characterization

Fig.2 shows the X-ray diffraction pattern of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ and the results of the Rietveld refinement[17]. The refined structural parameters are presented in Table 2. The obtained product was phase pure according to the X-ray powder diffraction. The chemical elements analyzed by titration and the crystal water measured by TG are shown in Table 3. The measured composition values fit well with the given formula.

In Fig.2, the X-ray diffraction pattern shows remarkable similarity to the pattern of $Ni[B_6O_7(OH)_6]\cdot 5H_2O$[18]. For comparability reasons, the standard crystallographic space group setting $P2_1/c$ of $Ni[B_6O_7(OH)_6]\cdot 5H_2O$ was kept for $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ (Element analysis: Mg 6.38%, B 15.99%, O 73.20%) leading to lattice parameters of a=0.898 87(3) nm, b=2.179 35(7) nm, c=0.720 79(2) nm, γ=99.8759(6)°, and V=1.391 07(8) nm^3.

In the crystal structure of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ (Fig.3), the asymmetric unit consists of one Mg atom, one $B_6O_7(OH)_6$ cluster and five H_2O molecules. The B atoms are in both 3- and 4-coordinated environments forming BO_3 triangles and BO_4 tetrahedra. Three BO_3 and three BO_4 units are connected by sharing a common O atom to form $B_6O_7(OH)_6$. The Mg atom is 6-coordinated with six O atoms to form a MgO_6 octahedron. In each units MgO_6 octahedron, the Mg atom shares two common O atoms with one $B_6O_7(OH)_6$ cluster and four common O atoms with four H_2O

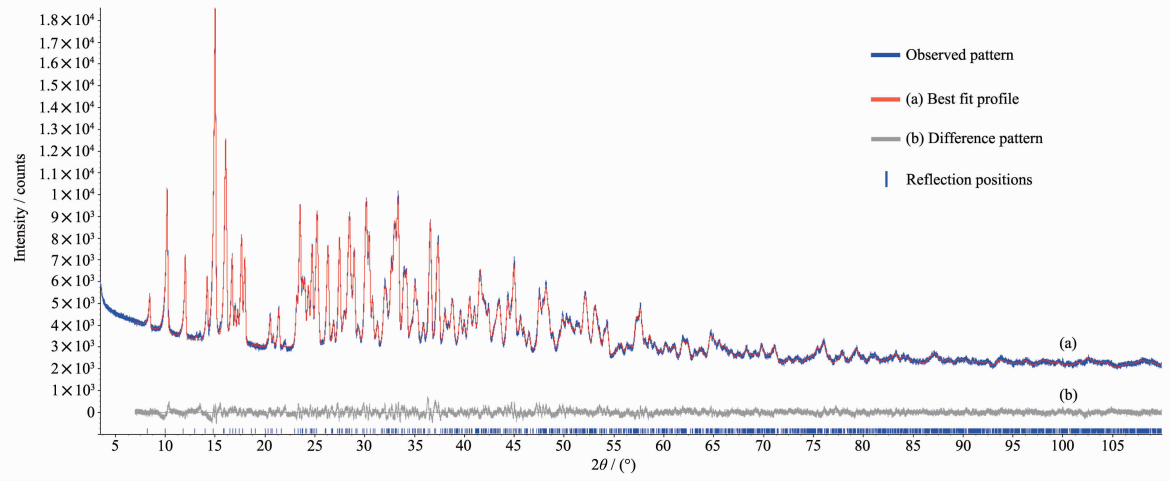

Fig.2 X-ray diffraction pattern of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ and results of the rietveld refinement

Table 2　Crystallographic and rietveld renement data for $Mg[B_6O_7(OH)_6]\cdot 5H_2O$

Empirical formula	$Mg[B_6O_7(OH)_6]\cdot 5H_2O$	a / nm	0.898 87(3)
Compound	Magnesium Borate	b / nm	2.179 35(7)
Formula weight	393.28	c / nm	0.720 79(2)
Starting angle 2θ / (°)	3.5	γ / (°)	99.875 9(6)
Final angle 2θ / (°)	110	Volume / nm^3	1.391 07(8)
Data collection / (s per step)	26.67	R_{Bragg} / %	1.67
Temperature / ℃	25	R_{exp} / %	2.62
Crystal system	Monoclinic	R_p / %	4.26
Space group	$P2_1/c$	R_{wp} / %	5.53
Z	4	No. of variables	100

Table 3　Titration analysis of the $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ phase

%

	MgO	B_2O_3	H_2O
Theoretical	10.25	53.11	36.65
Experimental	10.33	52.85	36.84

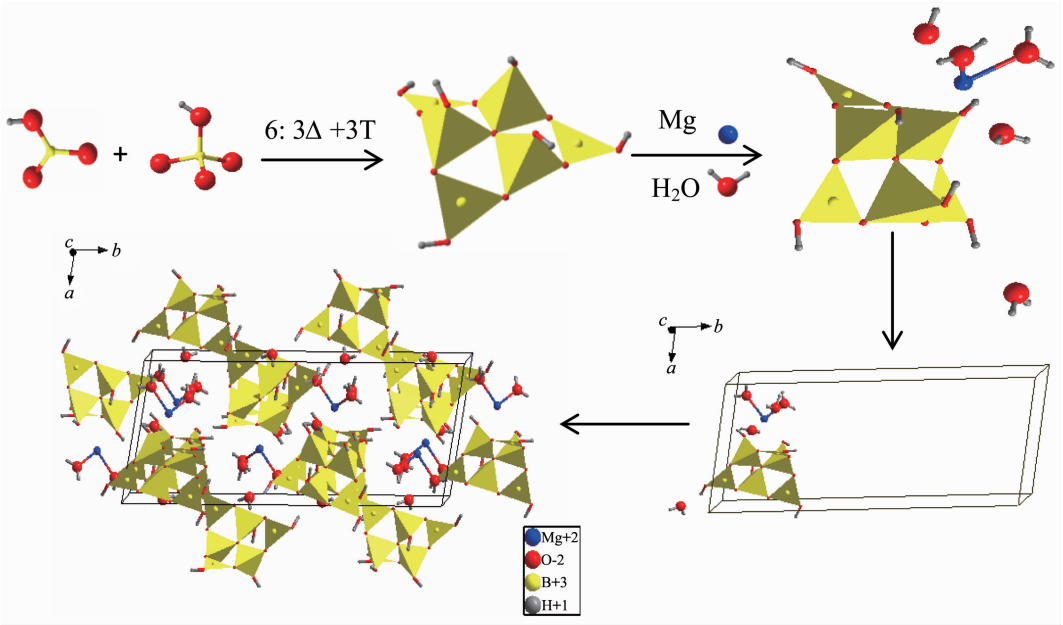

Fig.3　Crystal structure of the $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ compound

forming a 3D $Mg(H_2O)_4B_6O_7(OH)_6$ framework. Furthermore, the last one H_2O connects with the $Mg(H_2O)_4B_6O_7(OH)_6$ framework to form the whole structure of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$.

In the $B_6O_7(OH)_6$ cluster, the B-O distances of BO_3 triangles are in the range of 0.135 7~0.138 5 nm (average 0.136 8 nm), and the B-O distances of BO_4 tetrahedra are in the range of 0.143 8~0.152 4 nm (average 0.147 7 nm). The O-B-O angles of the BO_3 triangles and the BO_4 tetrahedra are in the range of 115.018°~122.712° and 107.226°~111.398°, respectively. The Mg-O distances are in the range of 0.203 5~0.213 7 nm. The bond distances and angles of the compound are in agreement with other borate compounds reported previously[19-21].

2.3　FTIR and raman spectroscopy

Fig.4 and Fig.5 show the FT-IR and Raman spectra of $Mg[B_6O_7(OH)_6]\cdot 5H_2O$, respectively. In the FT-IR spectrum, the bands at high wavenumbers of 3 200~3 600 cm^{-1} belonged to stretching of hydroxyl

(ν(O-H)); and the peak at 1 663 cm^{-1} corresponded to bending of H-O-H. According to literatures[11,22], The bands at 1 420, 1 350 cm^{-1} were assigned to asymmetric stretching of the three-coordinate boron ($\nu_{as}(B_{(3)}\text{-}O)$). The bending of B-O-H was observed at band of 1 253 cm^{-1}. The peaks between 1 174 and 1 053 cm^{-1} belonged to asymmetric stretching of four-coordinated boron ($\nu_{as}(B_{(4)}\text{-}O)$). The symmetric stretching of $B_{(3)}$-O and $B_{(4)}$-O was observed in the range of 807~944 cm^{-1}. And the band around 682 was out-of-plane bending of $B_{(3)}$-O.

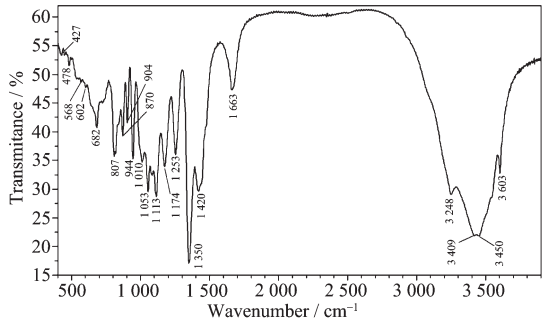

Fig.4 FT-IR spectrum of the $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ compound

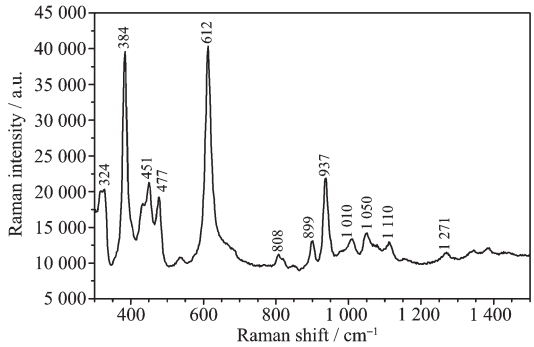

Fig.5 Raman spectrum of the $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ compound

In the Raman spectrum, based on the assignment of borates[22-24], weak bands in the region of 1 200~1 400 cm^{-1} and 1 110~1 000 cm^{-1} were asymmetric stretching of the three-coordinate boron ($\nu_{as}(B_{(3)}\text{-}O)$) and four-coordinate boron ($\nu_{as}(B_{(4)}\text{-}O)$), respectively. The band at 937 cm^{-1} was assigned to symmetric stretching of the three-coordinate boron ($\nu_s(B_{(3)}\text{-}O)$); and the bands around 899, 808 cm^{-1} were $\nu_s(B_{(4)}\text{-}O)$. Generally, the bands in the range of 610~650 cm^{-1} were associated with the symmetric pulse vibration of triborate anion or hexaborate anion[22]. In this study, the strong band at 612 cm^{-1} belonged to the characteristic peaks of $\nu_p(B_6O_7(OH)_6^{2-})$. Besides, the peaks at and below 477 cm^{-1} were assigned to bending of four-coordinate boron ($\delta(B_{(4)}\text{-}O)$).

3.4 Thermal analysis

TG and DSC analyses of the $Mg[B_6O_7(OH)_6]\cdot 5H_2O$ phase are shown in Fig.6. Three endothermic peaks (151, 211 and 994 ℃) and one exothermic peak (694 ℃) occurred in the DSC curve. In the first step, the weight loss is about 20% which was similar to the theoretical values of five water molecules weight of 22.90%, indicating there were five water molecules in the compound. In the second step, the weight loss was about 17%, which can be regarded as the weight of six hydroxyls (theoretical value of 13.75%) and the remaining water. The above total weight loss is about 37% corresponding to the weight of five water molecules and six hydroxyl (theoretical values of 36.65%) in the compound. In the third step, the structure of the compound was changed after removing five water molecules and six hydroxyl. The fourth step indicates the melting point of the calcined crystals.

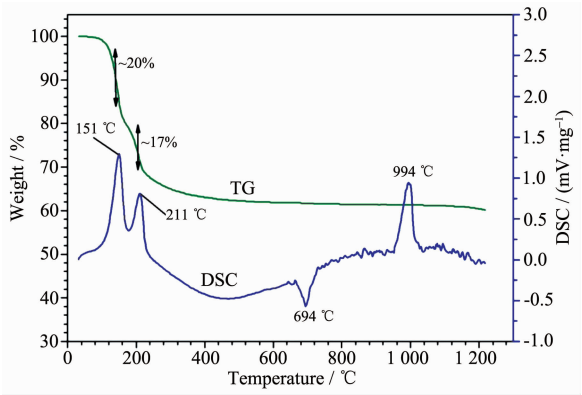

Fig.6 TG and DSC analyses of the $Mg[B_6O_7(OH]_6\cdot 5H_2O$ compound

To study the thermal decomposition behavior, the dehydrated products calcined at 400, 800 and 1 000 ℃ were confirmed by XRD analysis (Fig.7). Before XRD analysis, the dehydrated product calcined at 800 ℃ was treated with methanol solution by esterification reaction to remove B_2O_3 which occurred together with the dehydrated product during calcination process. In Fig.7, the exothermic peak around 694 ℃ marked the transition of the dehydrated amorphous product to

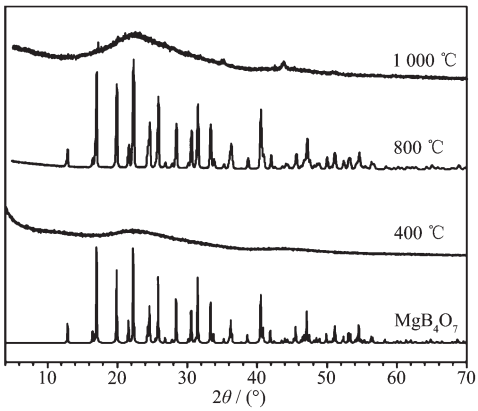

Fig.7　XRD patterns of dehydrated products

MgB_4O_7 (PDF card: 00-01-0927). While the calcined temperature went up to about 1 000 ℃, the MgB_4O_7 crystal began to melt and stuck in the alumina crucible during cooling process. Therefore, a whole decomposition process is presented by the following chemical reactions:

$MgB_6O_7(OH)_6 \cdot 5H_2O$ (crystal) →
$MgB_6O_7(OH)_6$ (amorphous)+$5H_2O$ (gas) (~160 ℃)
$MgB_6O_7(OH)_6$ (amorphous) →
MgB_6O_7 (amorphous)+$3H_2O$ (gas) (~400 ℃)
MgB_6O_7 (amorphous) →
MgB_4O_7 (crystal)+B_2O_3 (amorphous) (~700 ℃)
MgB_4O_7 (crystal) → MgB_4O_7 (liquid) (~994 ℃)

3.4　Results of optical measurements

Fig.8 shows the absorption spectrum of $Mg[B_6O_7(OH)_6] \cdot 5H_2O$ compound. The absorption data were calculated from the following Kubelka-Munk function: $F(R)=(1-R)^2/(2R)$, where R is the reflectance. The energy gap E_g was calculated by the function: $E_g=1\ 240/\lambda$, where λ is the wavelength. In Fig.8, the energy gap

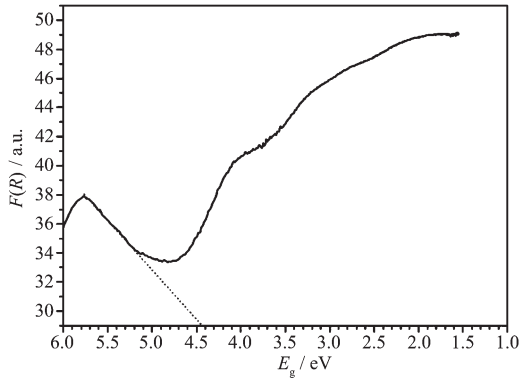

Fig.8　Optical absorption spectra of $Mg[B_6O_7(OH)_6] \cdot 5H_2O$ compound

E_g of $Mg[B_6O_7(OH)_6] \cdot 5H_2O$ compound determined from extrapolation of high energy part of absorption spectra is about 4.44 eV.

3　Conclusions

A new magnesium borate mineral, $Mg[B_6O_7(OH)_6] \cdot 5H_2O$ has been synthesized by dilution method from boron-bearing salt lakes for the first time at room temperature. The low reaction temperature used in this study provides a green chemistry approach for the synthesis of magnesium borate. The dilution crystallization method also provides a possible economic extraction of boron resources from salt lake brine. The crystal structure of this new compound was solved by laboratory X-ray powder diffraction data. The compound crystallizes in the monoclinic space group $P2_1/c$. Its crystal structure consists of infinite chains of $B_6O_7(OH)_6$ clusters, intercalated by MgO_6 and H_2O molecules, forming a 3D framework. The vibrational spectroscopy of FTIR and Raman reveals the presence of BO_3 triangles, BO_4 tetrahedra, water H_2O and the characteristic $B_6O_7(OH)_6^{2-}$ anion in the compound, which further verifies the structural characterization by X-ray powder diffraction. The thermal analysis (TG and DSC) showed that there were at least four phases occurred during decomposi-tion process. The thermal behavior goes through the transformation from amorphous to crystal phase of MgB_4O_7. The optical measurement found that the energy gap of the new magnesium borate is about 4.44 eV.

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