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Formation Mechanism and Thermodynamic Property of Basic Magnesium Chloride Whisker

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The basic magnesium chloride whiskers including type3-1-8, 3-1-6, 9-1-5 and 5-1-3 were synthesized simultaneously in the MgO-MgCl-H_2O solution system. The results agree well with the formation mechanism of that the unit of the crystal growth, anion or hydroxyl $[Mg–(OH)_y]^{2–y}$ ($1 \leq y \leq 6$) and $x[Mg–(OH)_2]$ ($1 \leq x \leq 9$) were the basic construction of basic magnesium chloride and the reaction temperature and molar ratio of $MgCl_2$ /MgO were the important effect factors. The standard molar enthalpies of basic magnesium chloride whisker (type 3-1-8) were obtained from a combination of the results with measured enthalpies of basic magnesium chloride whisker (type 3-1-8) in HCl(aq.) and together with the standard molar enthalpies of formation of MgO(s), $MgCl_2·6H_2O$ and H_2O(l) through the design of thermochemical cycle of basic magnesium chloride.

Keywords: Basic magnesium chloride, Whisker, Formation mechanism, Thermodynamic property.

INTRODUCTION

The general composition: $xMg(OH)_2·MgCl_2·yH_2O$ of the basic magnesium chlorides whiskers (called: type x-1-y) have been established by several authors since its discovery[1-3]. A lot of phase stoichiometries can be found that most remain unconfirmed, the basic magnesium chloride (BMC) including phase 2 (type 2-1-2 and type 2-1-4), phase 3 (type 3-1-1, type 3-1-6 and type 3-1-8), phase 5 (type 5-1-3, type 5-1-8 and type 5-1-12) and phase 9 (type 9-1-4, type 9-1-5 and type 9-1-8) have been reported. Among of them the type 3-1-8 phase with the formula $3Mg(OH)_2·MgCl_2·8H_2O$ and the type 5-1-8 phase with the formula $5Mg(OH)_2·MgCl_2·8H_2O$ were important and fundamental phase form which were extensive investigated below 100 °C[4-10] and with the formulas of type 2-1-2, type 2-1-4, type 3-1-1, type 9-1-4 and type 9-1-5 phases were founded only above 100 °C by thermal-method in the system MgO-$MgCl_2$-H_2O[11,12]. The phase composition of the basic magnesium chloride whiskers in the system MgO-$MgCl_2$-H_2O were complex and multiple, it is not only the difference of phase 2, 3, 5 and 9, but also the difference of the numbers of bounded water. The formation mechanism of the basic magnesium chloride whiskers in the system MgO-$MgCl_2$-H_2O were uncertain and inconsistent and focus on the type 3-1-8, type 5-1-8, as well as type 9-1-4 and the formation mechanism with regard to the others phase (especially as phase 2) and the bounding numbers of water were hardly any discussed. The initiation and growth process of the basic magnesium chloride in the system MgO-$MgCl_2$-H_2O includes phase transformation, morphology evolution, growth mechanism and crystal orientation in whisker synthesis. The amorphous magnesium hydroxide $[Mg–(OH)_2]$, Mg^{2+} and $Cl^–$ ions, $[Mg–(OH)_y]^{2–y}$ (y = 0, …6) anion coordination-polyhedras and H_2O were proposed as the basic units to form the basic magnesium chloride whiskers $xMg(OH)_2·MgCl_2·yH_2O$ according to the experiment of the dissolution of MgO and $MgCl_2$ in water and the coordination reaction of Mg^{2+} ions and $OH^–$. The molar ratio of MgO/$MgCl_2$, the concentration of Mg^{2+} in the solution, the value of pH in the solution system and the reaction temperature are the most important factors to effect the formation of phase form[13]. In this paper the basic magnesium chloride whiskers including type 3-1-6, type 3-1-8, type 5-1-3 and type 9-1-5 were synthesized simultaneously in the system MgO-$MgCl_2$-H_2O with difference reaction temperature from 50 to 100 °C and difference value of pH of solution from 4.2 to 6.8 only by adjusting the molar ratio of magnesium chloride hexahydrate and magnesium oxide respectively, the results agree well with and secondary provide a proof for the prediction of formation mechanism of basic magnesium chloride[13].

In comparison with the knowledge of structure chemistry and aqueous chemistry of basic magnesium chloride whisker, there is less understanding of thermodynamics properties of basic magnesium chloride in the literature. But the thermochemistry and thermodynamic properties of nanomaterials such as hydrate magnesium borate, nanoweeds ZnO, TiO_2, magnesium sulfate, magnesium silicates. Magne-sium oxide and beryllium have been reported[14-21], there will be providing important support for scale-up and controlling synthesis of the nanomaterial[22]. The thermodynamic properties of type 3-1-8 were studied through the design of thermochemical cycle of basic magnesium chloride in this paper firstly.

EXPERIMENTAL

1.2 g of magnesia oxide, 100 mL of distilled water was placed into a 250 mL. three-necked, round-bottomed flask in a constant temperature water bath provided with a electric stirrer, the water bath temperature was maintained at 50 °C, stirring speed was adjusted to 400 rpm, reaction for 40 min and then right amount of magnesium chloride hexahydrate was added many times to three-necked flask, The pH of solution is measured with a pH meter and reaction stopped until the desired pH of the solution reached and strike filter. The filtrate was sealed with plastic wrap and placed at-side for 48 h at room temperature, the precipitate was filtered and washed by distilled water and ethanol successively for several times and dried in the oven for 12 h at 80 °C, the sample was obtained, characterized and tested by SEM, XRD and TG.

1.72 g of basic magnesium chloride whisker (type 3-1-8) was metered the volume into a 250 mL volumetric flask, neutralization heat meter was set at power of 1.0 w, the sample was poured into the measuring instrument insulation device and then 40 mL of solution of hydrochloric acid (1 mol/L). It was join in ampoules, the neutralization heat meter was turn on until the little change of temperature, the result was recorded per 20 s when the ampoule bottle was open. It was powdered on when the result have a downward trend and the result was continued recorded until have a difference of 0.3 s between the data which the power was turn on after and before. The average result of the experiment repeated three times was used.

Diagram of the thermochemical cycle used to calculate the standard molar formation enthalpy, entropy and Gibbs free energy change of typical type 3-1-8 basic magnesium chloride whisker was shown in Fig. 1. The heat of neutralization associated solute in the solvent was measured by neutralization heat meter, the constant pressure heat capacity was calculated according to the eqn. 1:

$$\frac{Q_{neu.}}{\Delta T_{neu.}} = \frac{P \times t}{\Delta T_{e.}} \quad (1)$$

$Q_{neu.}$ = Constant pressure heat capacity (kJ); $\Delta T_{neu.}$ = Measured temperature difference; $\Delta T_{e.}$ = Difference of temperature *i.e.*, difference between the power was turn on after and before; P = pressure (Pa); t = temperature (K).

The enthalpy was equal to neutralization heat and to constant pressure heat capacity simultaneously as system for constant pressure in eqn. 1, the standard enthalpy change of reaction can be obtained from formula (2):

$$\Delta_r H_m^{\Theta}(4) = \Delta H / n(BMC) \quad (2)$$

n: molar number of basic magnesium chloride (BMC).

The standard molar reaction enthalpy of basic magnesium chloride was obtained by eqn. 3 combined with the standard molar reaction enthalpy of $MgCl_2$(s), $MgCl \cdot 6H_2O$(s) and H_2O(l) in NBS tables[23]:

$$\Delta_r H_m^{\Theta}(5) = \Delta_r H_m^{\Theta}(1) + \Delta_r H_m^{\Theta}(2) + \Delta_r H_m^{\Theta}(3) - \Delta_r H_m^{\Theta}(4) \quad (3)$$

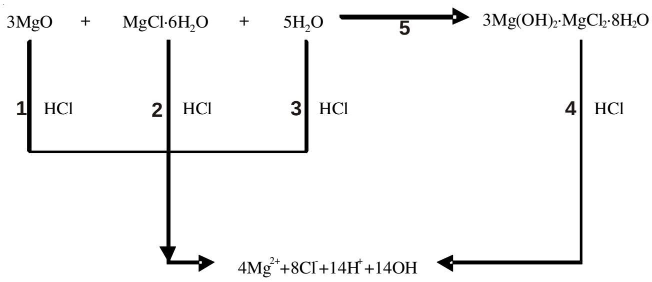

Fig. 1. Diagram of thermochemical cycle of basic magnesium chloride whisker

RESULTS AND DISCUSSION

Effect of pH of solution on morphology of samples: SEM image of effect of pH of solution on morphology of samples as reaction temperature maintained at 50 °C was shown in Fig. 2. It can be seen that there have been typical fiber morphology for all samples obtained when the pH of solution was between 5.3 to 6.8, only the diameter and length of the fiber was different, there has been cotton materials with the increased pH of solution until no fiber as the pH of solution over 6.8.

Effect of pH of solution and reaction temperature on morphology of samples: SEM image of effect of pH of solution and reaction temperature on morphology of samples was shown in Fig. 3. It can be seen that the pH of solution changed from 4.1 to 4.2, 4.3 to 4.7, 4.8, to 4.9 to 5.2, respectively as temperature changed from 100 °C, 90 °C, 70 °C, to 60 °C and there still have been typical fiber morphology with the increased reaction temperature to 100 °C and decreased pH of solution to 4.2.

XRD pattern of the samples with difference pH of solution: The XRD pattern of the samples with difference pH of solution were shown in Fig. 4. It can be seen that diffraction peak as 2θ at 7.958, 11.148, 21.604 and 37.376 was correspond well with the orthogonal structure of $9Mg(OH)_2 \cdot MgCl_2 \cdot 5H_2O$ in standard PDF card (JCPDS-33-0859) when pH of solution was 4.5 and 5.3 in Fig. 3 and as 2θ at 10.860, 14.827, 21.819, 22.962, 24.992, 32.964 and 36.572 was correspond well with the orthogonal structure of $3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O$ when pH of solution was 4.9 5.4, 5.6, 6.0 and 6.7 and as 2θ at 13.233, 21.657, 24.502, 29.756, 33.981, 34.209, 36.464 was correspond well with the orthogonal structure of $3Mg(OH)_2 \cdot MgCl_2 \cdot 6H_2O$. When pH of solution was 6.4 and as 2θ at 10.860, 21.819, 58.887 was correspond well with the orthogonal structure of $5Mg(OH)_2 \cdot MgCl_2 \cdot 3H_2O$ when pH of solution was 6.8 and 2θ at 18.527, 32.877, 37.983, 50.875, 62.114, 72.096 was correspond well with the orthogonal structure of $Mg(OH)_2$ when pH of solution was 6.8.

TG pattern of the samples with difference pH of solution: TG pattern of the samples with difference pH of solution was shown in Fig. 5, it can be seen that there have been the typical multistage dehydration for all samples with difference pH of solution, it can be approximatively divided into three groups, one side, there are much more water or hydroxyl in type 9-1-5, than in type 3-1-8 and in type 3-1-6 according to the difference of multistage dehydration when pH of solution was 5.3 than 5.4, 6.0, 6.7 and 4.5 and 6.4, respectively, on the other side, it confirmed that the high reaction temperature was in favour of formation of magnesium hydroxyl. the difference of multistage dehydration of pH of solution 5.4, 6.0 and 6.7 was nearly equal,

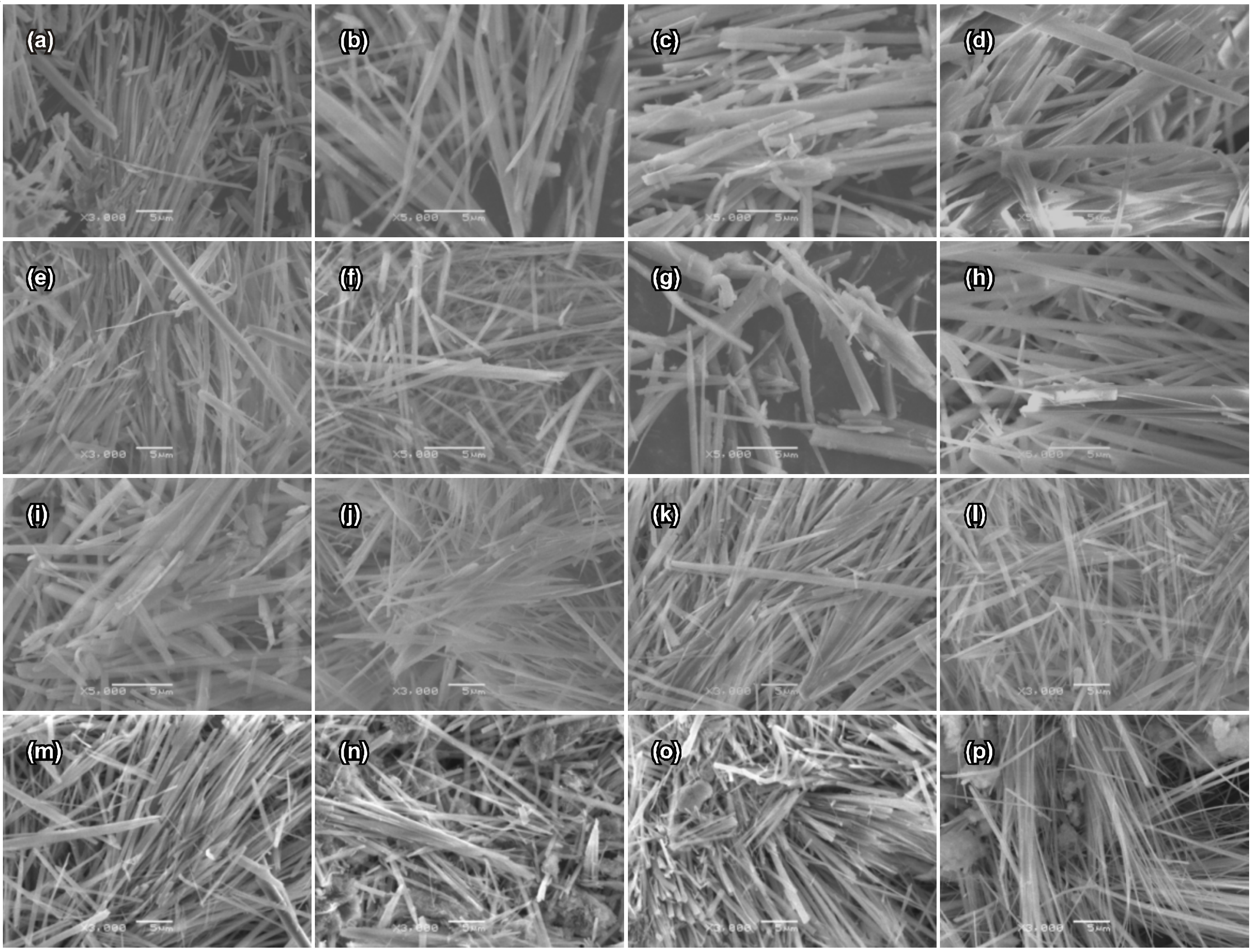

Fig. 2. SEM image of effect of pH of solution on morphology of samples; pH of solution: (a) 5.3, (b) 5.4, (c) 5.5, (d) 5.6, (e) 5.7, (f) 5.8, (g) 5.9, (h) 6.0, (i) 6.1, (j) 6.2, (k) 6.3, (l) 6.4, (m) 6.5, (n) 6.6, (o) 6.7, (p) 6.8

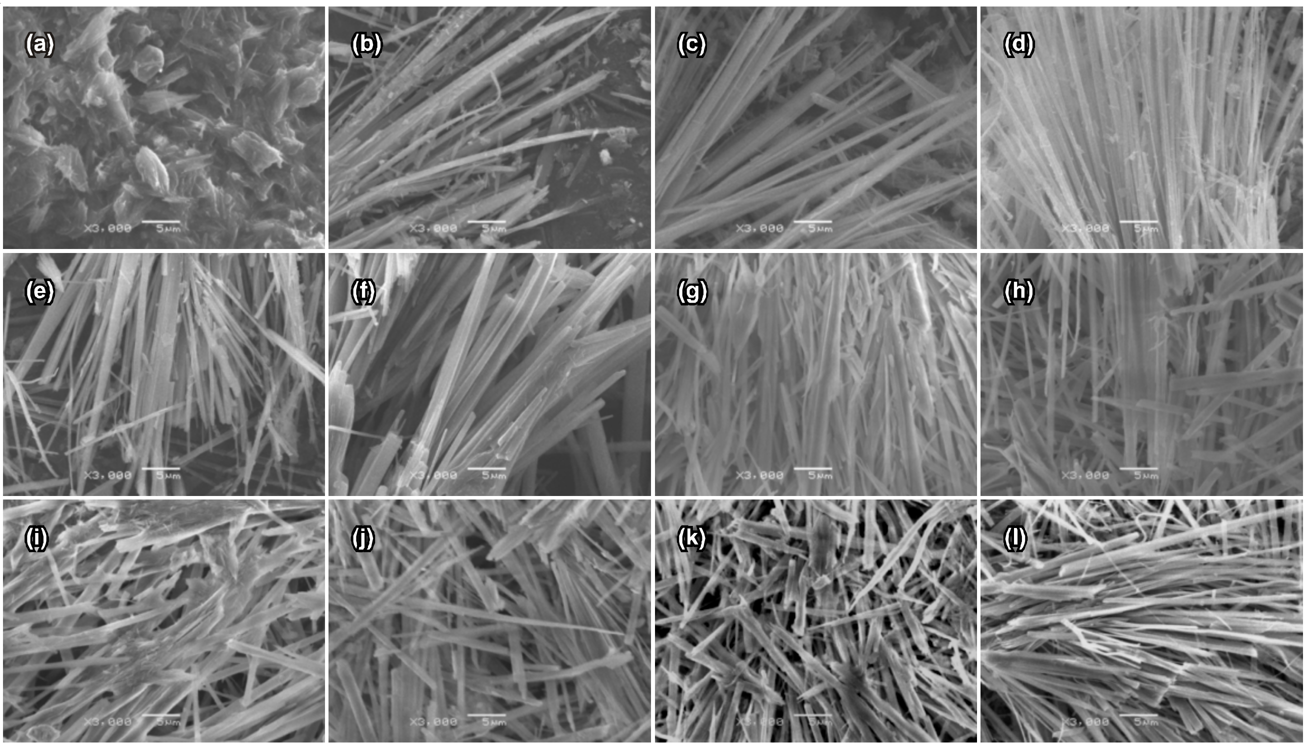

Fig. 3. SEM image of effect of pH of solution and reaction temperature on morphology of samples; pH of solution and reaction temperature: (a) 4.1, (b) 4.2, 100 °C, (c) 4.3, (d) 4.4, (e) 4.5, (f) 4.6, (g) 4.7, 90 °C, (h) 4.8, 70 °C, (i) 4.9, (j) 5.0, (k) 5.1, (l) 5.2, 60 °C

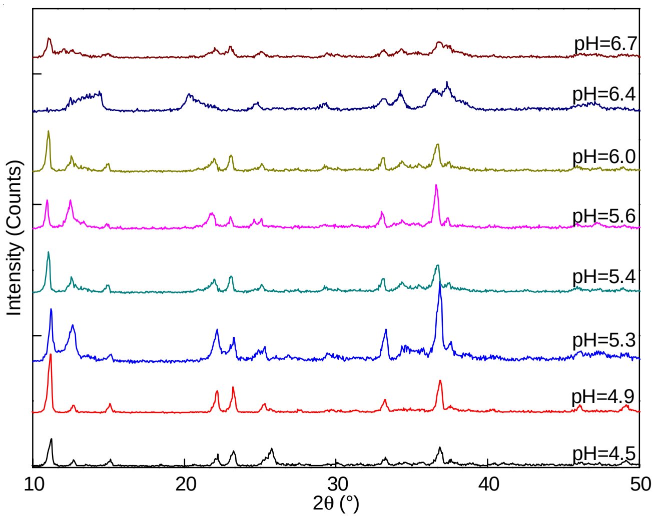

Fig. 4. XRD pattern of the samples with difference pH of solution; pH of solution: (a) 4.5, (b) 4.9, (c) 5.3, (d) 5.4, (e) 5.6, (f) 6.0, (g) 6.4, (h) 6.7, (i) 6.8

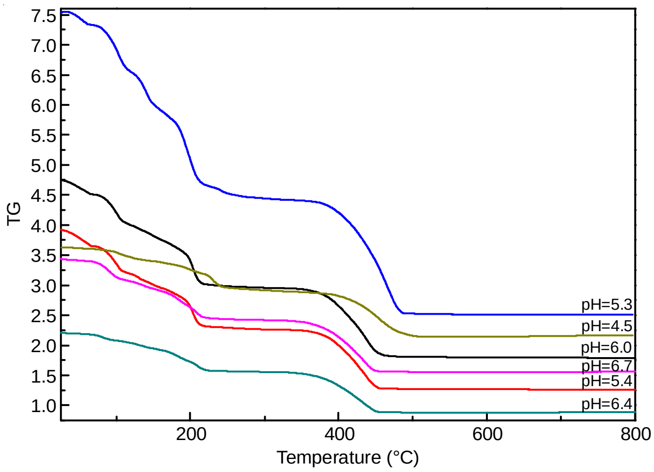

Fig. 5. TG pattern of the samples with difference pH of solution

it correspond well with the result by XRD analytical, that is belong to same structure of sample.

Formation mechanism of polymorphous of basic magnesium chloride: The crystallization growth units includes $[Mg–(OH)_2]$, $[Mg–(OH)_y]^{2–y}$, $Cl^–$, $OH^–$ and H^+ and the formation of $xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O$ depended on the molar ratio of $MgCl_2/Mg_2O$, the concentration of Mg^{2+} ions, the pH value of the solution system and the reaction temperature in eqns. 4 or 5.

$$x[Mg–(OH)]^+ + xOH^– + [Mg–(OH)_y]^{2–y} + 2Cl^– + yH^+ \longrightarrow xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O \quad (4)$$

$$x[Mg–(OH)_2] + [Mg–(OH)_y]^{2–y} + 2Cl^– + yH^+ \longrightarrow xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O \quad (5)$$

The type 9-1-5 can be obtained while 9 times x and 5 times y as eqn. 6 decided in eqn. 5:

$$9[Mg–(OH)_2] + [Mg–(OH)_5]^{3–} + 2Cl^– + 5H^+ \longrightarrow 9Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O \quad (6)$$

The type 3-1-8 can be obtained while 3 times x and y equals 8 as eqn. 7 decided in eqns. 4 or 5:

$$3[Mg–(OH)] + 3OH^– + [Mg–(OH)_8]^{3–} + 2Cl^– + 8H^+ \longrightarrow 3Mg(OH)_2{\cdot}MgCl_2{\cdot}8H_2O \quad (7)$$

The type 3-1-6 and type 5-1-3 can be obtained as eqns. 8 and 9:

$$3[Mg–(OH)]^+ + 3OH^– + [Mg–(OH)_6]^{4–} + 2Cl^– + 6H^+ \longrightarrow 3Mg(OH)_2{\cdot}MgCl_2{\cdot}6H_2O \quad (8)$$

$$5[Mg–(OH)_2] + [Mg–(OH)_3]^– + 2Cl^– + 3H^+ \longrightarrow 5Mg(OH)_2{\cdot}MgCl_2{\cdot}5H_2O \quad (9)$$

The concentration or molar ratio of $MgCl_2/H_2O$ and the reaction temperature in the system of MgO-$MgCl_2$-H_2O seriously affect the form of the basic magnesium chloride whiskers $xMg(OH)_2{\cdot}MgCl_2{\cdot}yH_2O$. The results agree well with that the higher temperature and the pH of solution, the amorphous hydroxide was the mainly crystallization growth unit and , on the contrary. (y = 0, …6) anion coordination-polyhedras was always the basic crystalli-zation growth unit and change with the pH of solution.

Thermodynamic properties of type 3-1-8 of basic magnesium chloride: The enthalpy was equal to neutralization heat and to constant pressure heat capacity simultaneously as system for constant pressure in eqn. 1 and standard enthalpy change of reaction can be obtained from eqn. 2, the results was listed in Table-1, it can be seen that the average result of 1284.274 kJ of constant pressure heat capacity and 308.2258 kJ/mol of standard enthalpy change of reaction were obtained.

TABLE-1
$Q_{neu.}$ AND $\Delta_r h_m^{\ominus}$ OF TYPE 3-1-8 OF BASIC MAGNESIUM CHLORIDE AT 298.15 K

No.	$Q_{neu.}$(kJ)	$\Delta_r H_m^{\ominus}$ (kJ/mol)
1	1406.240	337.4976
2	1216.582	291.9797
3	1230.000	295.2000
Average	1284.274	308.2258

The standard molar enthalpy, Gibbs free energy, entropy and constant pressure heat capacity of reactant in the solution were shown in Table-2.

TABLE-2
DATA OF STANDARD MOLAR ENTHALPY, GIBBS FREE ENERGY, ENTROPY AND CONSTANT PRESSURE HEAT CAPACITY OF REACTANT IN THE SOLUTION

Material	$\Delta_f H_m^{\ominus}$ (kJ mol^{-1})	$\Delta_f G_m^{\ominus}$ (kJ mol^{-1})	$S_m^{\ominus}$ (J mol^{-1} k^{-1})	$C_{p,m}^{\ominus}$ (J mol^{-1} k^{-1})
H^+	0	0	0	0
Cl^-	-167.159	-131.228	56.5	-136.4
OH^-	-229.994	-157.244	-10.75	-148.5
Mg^{2+}	-466.85	-454.8	-138.1	
HCl(l)	-92.307	-95.299	186.908	29.12
H_2O(l)	-285.830	-237.129	69.91	75.291
MgO(S)	-601.70	-569.43	26.94	37.15
$MgCl_2$	-641.32	-591.79	89.62	71.38
$Mg(OH)_2$	-924.54	-833.51	63.18	77.03

The standard molar enthalpies of formation of the reactants in the thermochemical cycle was shown in Table-3, the standard molar enthalpies of formation of the reactants: MgO(s), $MgCl{\cdot}6H_2O$(s) and H_2O(l) and enthalpy of dissolution of aqueous hydrochlorice acid: HCl(aq.) were taken from the NBS tables.

TABLE-3
STANDARD MOLAR ENTHALPIES OF FORMATION OF THE REACTANTS IN THE THERMOCHEMICAL CYCLE

No.	Reaction	$\Delta_r H_m^\Theta$ (kJ mol^{-1})
1	$3MgO + 6HCl = 3MgCl_2 + 3H_2O$	-140.8360
2	$MgCl_2 \cdot 6H_2O + HCl = MgCl_2 + HCl \cdot 6H_2O$	-91.3600
3	$5H_2O + HCl = HCl \cdot 5H_2O$	-76.1400
4	$3Mg(OH)_2 \cdot MgCl_2 \cdot 8H_2O + 6HCl = 4Mg^{2+} + 8Cl^- + 14H^+ + 14OH^-$	337.4976
5	$3MgO + MgCl_2 \cdot 6H_2O + 5H_2O = 3MgCl_2 \cdot Mg(OH)_2 \cdot 8H_2O$	645.8336

The enthalpy of reaction $\Delta_r H_m^\Theta$ (5) and standard molar enthalpy of formation $\Delta_f H_m^\Theta$ of basic magnesium chloride were obtained combined with Table-2 and thermochemical cycle, the results were shown in Table-4 and the standard molar enthalpy of formation $\Delta_f H_m^\Theta$ of basic magnesium chloride was -6344.833 kJ mol^{-1}.

TABLE-4
ENTHALPY OF REACTION AND STANDARD MOLAR ENTHALPY OF FORMATION OF BASIC MAGNESIUM CHLORIDE

No.	$\Delta_r H_m^\Theta$ (5) (kJ mol^{-1})	$\Delta_f H_m^\Theta$ (kJ mol^{-1})
1	-645.8336	-6364.104
2	-600.3157	-6333.586
3	-603.5360	-6336.806
Average	-616.5618	-6344.833

The entropy difference of 256.388 J/k calculated by integration proved that the reaction process was an irreversible. Afterwards the Gibbs free energy change of -5003.457 J indicated that the reaction is carried out spontaneously.

Conclusion

The basic magnesium chloride whiskers including type 3-1-8, 3-1-6, 5-1-4 and 9-1-5 were synthesized simultaneously in the MgO-MgCl-H_2O solution system, the formation mechanism of the basic magnesium chloride obtained revealed that the anion or hydroxyl $[Mg–(OH)_y]^{2-y}$ ($1 \le y \le 6$) and x[Mg–$(OH)_2$] ($1 \le x \le 9$), were the unit of the crystal growth, the formation of basic magnesium chloride was effected by the molar ratio of $MgCl_2$/MgO and reaction temperature. The standard molar enthalpies of basic magnesium chloride whisker (type 3-1-8) were obtained from a combination of the results with measured enthalpies of basic magnesium chloride whisker (type 3-1-8) in HCl(aq.) and together with the standard molar enthalpies of formation of MgO(s), $MgCl_2 \cdot 6H_2O$ and H_2O(l) through the design of thermochemical cycle of basic magnesium chloride.

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