



A new method of preparing anhydrous magnesium carbonate (MgCO₃) under high pressure and its thermal property



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ABSTRACT

By using magnesium carbonate tri-hydrates (MgCO₃·3H₂O) as starting material, anhydrous magnesium carbonate (MgCO₃) was successfully synthesized by dehydration method under high pressure for the first time. The property of as-synthesized sample was investigated by powder X-ray diffraction (XRD) and Raman spectroscopy, respectively. The high pressure synthesis was performed at the various conditions to ensure that the optimal condition is 3 GPa and 800 °C for 1 h, and it is reasonable to explain the principle of MgCO₃ synthesis under high pressure. The size of micro-particles observed from Scanning Electron Microscope (SEM) image exceeds to 100 μm. As a good and important flame retardant material, its thermal property is investigated by Thermogravimetric (TG) analysis, Differential Scanning Calorimeter (DSC) measurement and high temperature X-ray diffraction (XRD) refinement, and the endothermic heat (128.59 KJ/mol), the thermal expansion coefficient along c-axis ($\alpha_c = 1.639 \times 10^{-5}/^\circ\text{C}$), the thermal expansion coefficient along the a-axis ($\alpha_a = 4.632 \times 10^{-6}/^\circ\text{C}$) and the volume thermal expansion coefficient ($\alpha_V = 2.576 \times 10^{-5}/^\circ\text{C}$) was quantified.

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1. Introduction

As a multifunctional material, magnesium carbonate (MgCO₃) has been the subject of extensive studies as the result of its extensive application and research value [1–6]. MgCO₃ is in industry regarded as one of important additive, which is mainly put in use as medicine, food, rubber industry, etc. Recently, MgCO₃ has attracted more attention as a new product of inorganic flame retardant [7,8]. Compared to the traditional flame retardants, it has the advantages of good thermal absorption, fire extinguishing property from releasing CO₂ and pollution-free for the environment. In the research fields of geoscience, MgCO₃, called as magnesite, is an important Mg-bearing mineral, and in these years the interest in carbonate minerals has grown significantly because the global carbon cycle has been a subject of great concern. In the interior of the earth, especially in the lower mantle environment, carbon exists mainly in the form of carbonate, iron carbides, carbon-bearing fluid, diamond, etc. Among these carbon-bearing minerals, magnesite has been reported to be stable under the temperature and pressure conditions of the earth's lower mantle.

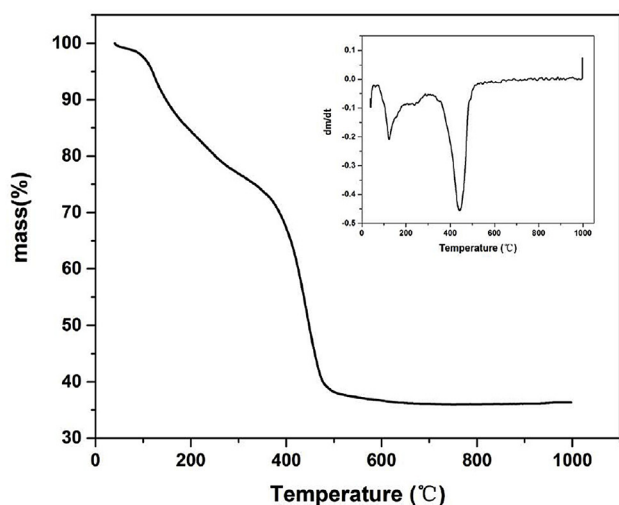
Thus, magnesite is expected to be a stable deep-carbon host at the lower mantle and its geochemistry and geophysics property can play a significant role in the global deep carbon recycle. For this reason, the magnesite is focused to study its thermal stability, P-V-T equation of state, chemical properties, etc. [9–11].

However, there has been almost no ready-made MgCO₃ product for experimental research to ensure high quality and high purity, because it is difficult to be properly prepared at ambient conditions. Actually the specification of magnesium carbonate available in the current market is typically associated with magnesium carbonate hydrates and basic magnesium carbonate. Besides, the natural mineral magnesite always contains varying quantities of Fe²⁺ and Mn²⁺ impurities, which can not up to the research standard of the analytical reagent. Hence it needs to explore the techniques for MgCO₃ synthesis in laboratory.

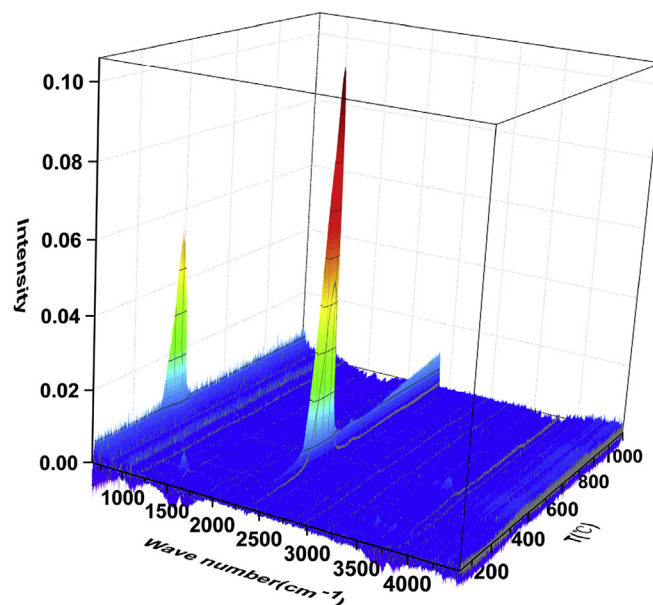
In the previous studies, different methods were reported to synthesize MgCO₃ [12–15]. Though MgCO₃ sample was obtained successfully by these methods, there were still some obvious deficiencies. The micro-particles sizes is too small to satisfy the basic requirement of micro-analysis, including micro-constitution and micro-composition analysis. Besides, it is worth considering to explore a new method to simplify processes and improve efficiency of MgCO₃ artificial synthesis.

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(a)



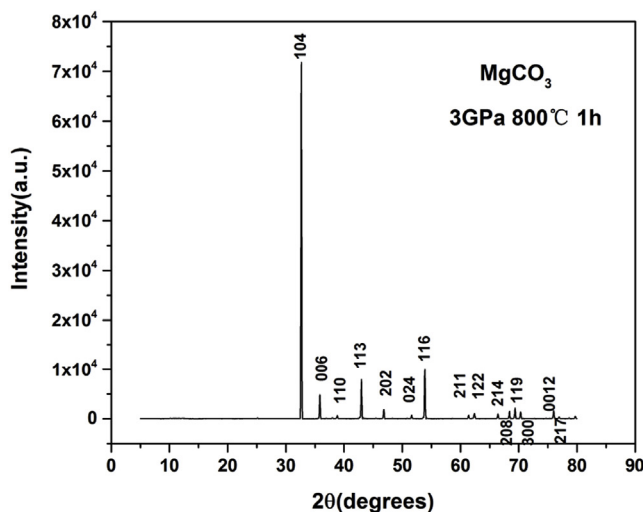
(b)

Fig. 1. (a) $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ TG analysis with $5^\circ\text{C}/\text{min}$ in argon atmosphere. (b) The evolved gas in the TG process analyzed by in-situ infrared spectrum.

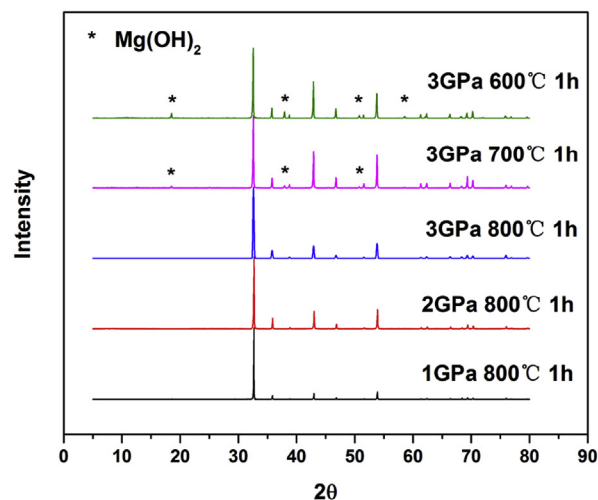
In this paper, we report a new and simple method of preparing MgCO_3 by dehydration method under high pressure and high temperature. The sample was identified by XRD as MgCO_3 single phase without any impurities. Significantly, the crystallinity quality is greatly improved with the micro-particles sizes exceeding to $100\ \mu\text{m}$, and the reaction time is controlled within 1 h so that the efficiency of the synthesis has been greatly improved. As a good flame retardant material, its thermal property was investigated by TG, DSC and high temperature XRD. Meanwhile, the decomposing heat quantity as well as the thermal expansion coefficient was measured.

2. Experiments

The starting material $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ (99.9%) was ground in an agate mortar with acetone. The sample pellet was made and sealed into a silver capsule of 6 mm in diameter and 3 mm length. Using NaCl as pressure medium, the high pressure synthesis was performed on a DS $6 \times 600\text{t}$ cubic-anvil-type apparatus with 23.5 mm truncation edge length of WC anvils, and its pressure was calibrated by Bi phase transition and chloride (LiCl , KCl and NaCl) melting curves at high pressure. Graphite heater (10 mm inner diameter and 14 mm outer diameter) and K-type thermocouple were used in



(a)



(b)

Fig. 2. (a) X-ray powder diffraction for the sample MgCO_3 synthesized at 3 GPa and 800°C for 1 h, using Si (99.999%) as zero-offset calibration. (b) X-ray powder diffraction for a series of samples synthesized under the various conditions. The impurity marked by * is identified as $\text{Mg}(\text{OH})_2$.

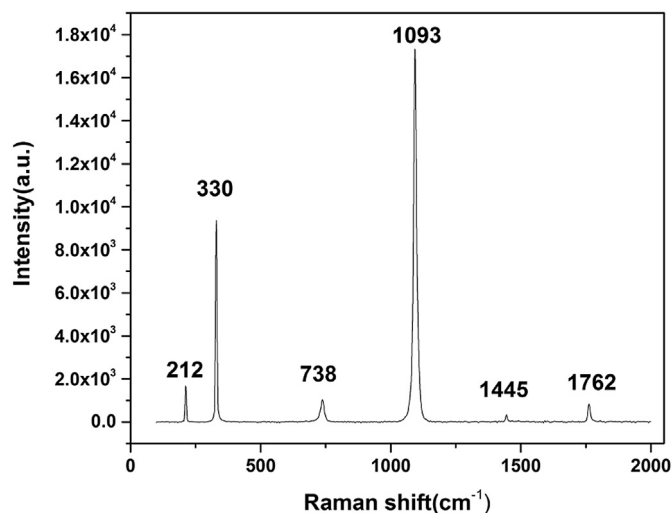


Fig. 3. Raman spectrum of as-synthesized MgCO_3 sample.

our experiments. The conditions with the various pressure and temperature were used for trial synthesis. Then it was quenched to room temperature and released the pressure slowly. Upon cleaned up the silver coverage, the sample was obtained.

As regard the decomposition process on the starting material $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$, the TG analysis as well as in-situ infrared spectrum detection were carried out and the result was shown in Fig. 1. A series of samples under various conditions were achieved and the phases identified by XRD were given in Fig. 2. Raman spectrum of as-synthesized MgCO_3 in the wavelength range of 100–2000 cm^{-1} was given in Fig. 3. The SEM image of MgCO_3 micro-particles was shown in Fig. 4. The results of TG and DSC analysis of as-synthesized MgCO_3 was shown in Fig. 5.

In the thermal analysis process, TG and DSC were determined by a simultaneous thermal analyzer (model: STA 449F3, NETZSCH, Germany). The sample (20 mg) was heated from 40 °C (5 °C/min heating rate) in argon atmosphere. Evolved gas analysis was performed by coupling STA with Fourier transform infrared spectroscopy (Vertex 70, Bruker, Germany). The infrared spectra of evolved gases were collected in the mid-infrared range (400–4000 cm^{-1}) using a resolution of 4 cm^{-1} and an accumulation of 16 scans [16].

High temperature XRD data was collected on a Panalytical multifunction X-ray diffractometer (model: Empyrean), equipped with an Anton Paar high temperature accessory (APHTK-16N). The heating process and high temperature XRD of as-synthesized

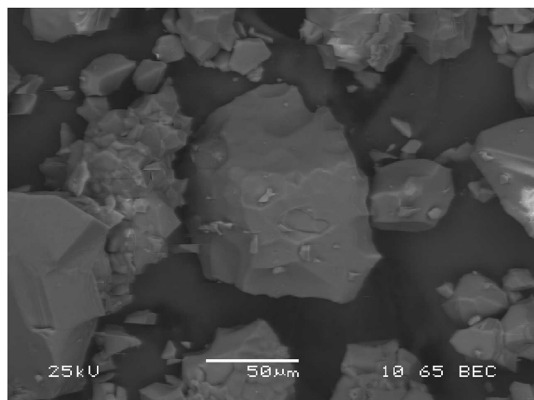


Fig. 4. The SEM image of MgCO_3 micro-particles.

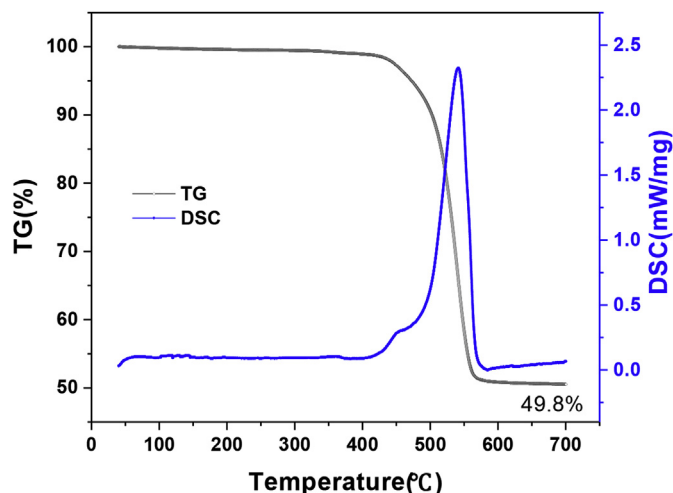


Fig. 5. The TG and DSC analysis of MgCO_3 .

MgCO_3 was performed below its decomposed temperature. Using Jade 6.5 XRD analysis software, the crystal structure parameters and unit cell volume have been refined from XRD data collected from 25 to 400 °C with 20 °C per step, and the thermal expansion coefficient is calculated and the results was shown in Table 1 and Fig. 6.

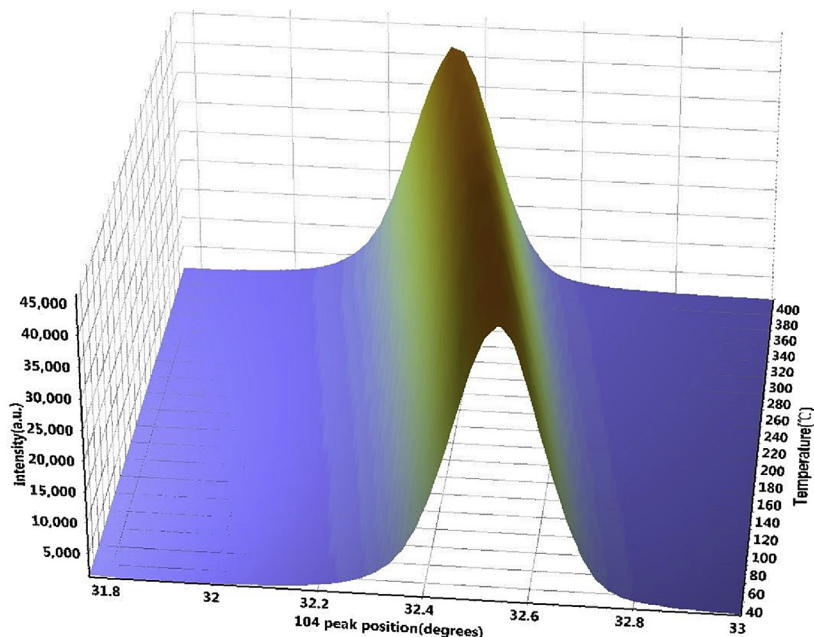
3. Result and discussion

Fig. 1(a) shows the TG decomposition process of $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at the heating rate of 5 °C/min in argon atmosphere. A sustained weight reduction was indicated from the TG curve shown in Fig. 1(a) and the evolved gas in the TG process was accurately analyzed by in-situ infrared spectrum shown in Fig. 1(b). Fig. 1(b) shows the relationship between the wave number (400–4000 cm^{-1}), temperature (40–1000 °C) and infrared absorption for the evolved gas. It is observed that H_2O infrared absorption peaks (located at around 400 cm^{-1}) and CO_2 infrared absorption peaks (located at around 2200 cm^{-1}) appeared at the temperature range from 100 °C to 1000 °C. It means that the loss of H_2O and CO_2 was taking place from 100 °C to 1000 °C all the time,

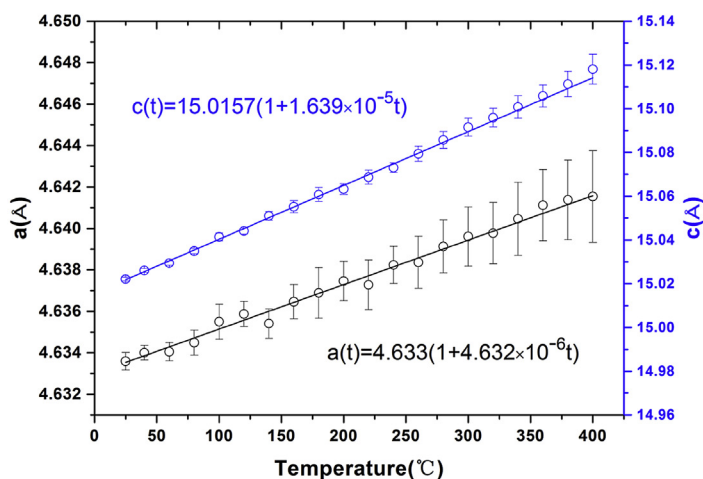
Table 1

The result of the parameters of MgCO_3 refined from XRD dates at various temperature, where σ_a , σ_c and σ_V is the error bar of the parameters a , c and V .

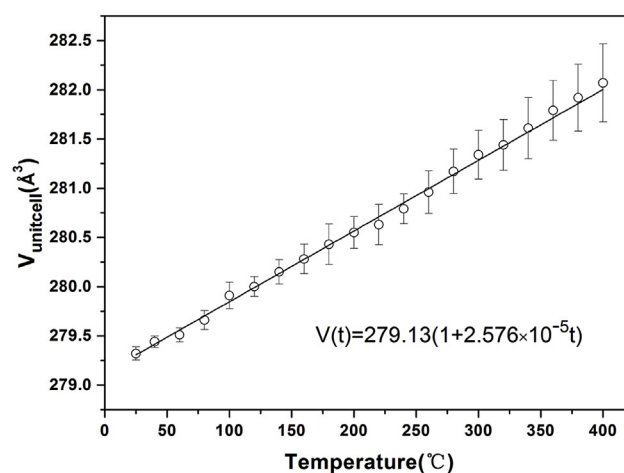
	$A(\text{Å})$	$\sigma_a(\text{Å})$	$c(\text{Å})$	$\sigma_c(\text{Å})$	$V(\text{Å}^3)$	$\sigma_V(\text{Å}^3)$
25 °C	4.63359	0.00042	15.02211	0.00091	279.32	0.07
40 °C	4.63400	0.00035	15.02604	0.00086	279.44	0.06
60 °C	4.63405	0.00044	15.02941	0.00101	279.51	0.07
80 °C	4.63449	0.00060	15.03489	0.00128	279.66	0.10
100 °C	4.63550	0.00084	15.04139	0.00179	279.91	0.14
120 °C	4.63587	0.00061	15.04408	0.00141	280.00	0.10
140 °C	4.63541	0.00071	15.05099	0.00200	280.15	0.12
160 °C	4.63646	0.00083	15.05517	0.00271	280.28	0.15
180 °C	4.63689	0.00122	15.06074	0.00318	280.43	0.21
200 °C	4.63746	0.00096	15.06325	0.00243	280.55	0.16
220 °C	4.63728	0.00120	15.06867	0.00322	280.63	0.20
240 °C	4.63824	0.00090	15.07302	0.00222	280.79	0.15
260 °C	4.63836	0.00125	15.07940	0.00349	280.96	0.22
280 °C	4.63913	0.00128	15.08570	0.00385	281.17	0.23
300 °C	4.63961	0.00143	15.09151	0.00405	281.34	0.25
320 °C	4.63977	0.00148	15.09587	0.00424	281.44	0.26
340 °C	4.64046	0.00176	15.10074	0.00518	281.61	0.31
360 °C	4.64112	0.00172	15.10581	0.00508	281.79	0.30
380 °C	4.64138	0.00192	15.11125	0.00574	281.92	0.34
400 °C	4.64154	0.00221	15.11805	0.00681	282.07	0.40



(a)



(b)



(c)

Fig. 6. (a) The (104) peaks shift to low angle while MgCO_3 heating. (b) The correlation between the parameters of MgCO_3 and the temperature. (c) The relationship between the unitcell volume of MgCO_3 and the temperature.

which indicates that $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ prefers to form basic magnesium carbonate as the formula of $x\text{MgCO}_3 \cdot y\text{Mg}(\text{OH})_2 \cdot z\text{H}_2\text{O}$. The final TG content was stabilized about at 36%, which is much greater than theoretical value 29% calculated by MgO . To achieve the final decomposition product MgO , the heating time at 1000°C must be rather long until both H_2O and CO_2 were lost completely. By understanding the TG result, it is confirmed that the compound $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ contains constitutional water not crystalliferous water, and thus because of the complex hydrolysis reaction, it is almost impossible to obtain MgCO_3 by heating $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ at the ambient conditions.

Under high pressure, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ hydrolysis reaction can be suppressed due to MgCO_3 high pressure stability. The crystal structure of sample synthesized at 3 GPa and 800°C for 1 h was analyzed by powder XRD as given in Fig. 2(a) and all the diffraction

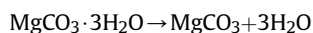
peaks can be indexed as MgCO_3 rhombohedral structure. We obtain the structure data of as-synthesized MgCO_3 with the space group $R\bar{3}c$ (no.167) and refine the lattice parameters with $a = 4.6336(4) \text{ \AA}$, $c = 15.0221(9) \text{ \AA}$.

The powder XRD result of a series of samples under various reaction conditions were shown in Fig. 2(b). At the condition of 1–3 GPa and 800°C for 1 h, the as-synthesized samples were identified as MgCO_3 without any impurity. Keeping 3 GPa, the impurity identified as $\text{Mg}(\text{OH})_2$ was observed at 600°C and 700°C while it was increasing with the reaction temperature reducing, which is implied that MgCO_3 is obviously more stable than $\text{Mg}(\text{OH})_2$ at high temperature and high pressure conditions and the phase of basic magnesium carbonate can not be observed under high pressure to be replaced by a phase separating as MgCO_3 and $\text{Mg}(\text{OH})_2$. Thus, $\text{MgCO}_3 \cdot 3\text{H}_2\text{O}$ hydrolysis reaction can be effectively

Table 2The thermal expansion coefficient α of MgCO_3 at the ambient pressure in the previous studies, where $\alpha = \alpha_0 + \alpha_1 T$.

Composition	α_a	α_c	α_v	Reference
MgCO_3	$\alpha_0 = 4.63 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$	$\alpha_0 = 1.64 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$	$\alpha_0 = 2.58 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$	This work
$(\text{Mg}_{0.984}\text{Mn}_{0.008}\text{Fe}_{0.007}\text{Ca}_{0.001})\text{CO}_3$	$\alpha_0 = 6.75 \times 10^{-6} \text{ } ^\circ\text{C}^{-1}$	$\alpha_0 = 2.29 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$	$\alpha_0 = 4.69 \times 10^{-5} \text{ } ^\circ\text{C}^{-1}$	[20]
$(\text{Mg}_{0.975}\text{Fe}_{0.015}\text{Mn}_{0.006}\text{Ca}_{0.004})\text{CO}_3$			$\alpha_0 = 4.03(7) \times 10^{-5} \text{ } \text{K}^{-1}$	[21]
			$\alpha_1 = 0.49(10) \times 10^{-8} \text{ } \text{K}^{-2}$	

and completely suppressed by controlling the pressure and especially temperature, and the process is described simply as follows:



As shown in Fig. 3, Raman spectrum of MgCO_3 in the wavelength range of 100–2000 cm^{-1} are dominated by the peaks located at 212, 330, 738, 1093, 1445 and 1762 cm^{-1} , in which the Raman peaks are fit with a Lorentzian function. There are six Raman active modes (T, L, ν_4 , ν_1 , ν_3 , $2\nu_2$), which are the vibration bands of calcite-type materials [17,18]. The peaks at 212 cm^{-1} comes from translational lattice mode T. The peak at 330 cm^{-1} is derived mainly from librational lattice mode L. The peaks at 738 cm^{-1} comes from in-plane bending internal mode ν_4 . The peak with the strongest feature located at 1093 cm^{-1} is caused by symmetric stretching internal mode ν_1 . Similarly, the peaks at 1445 and 1762 cm^{-1} are attributable the anti-symmetric stretching mode ν_3 and out-of-plane bend $2\nu_2$, respectively.

Fig. 4 shows the SEM image of MgCO_3 micro-particles. It can be seen clearly that the as-synthesized MgCO_3 consists of the various size of micro-particles and the maximum size of micro-particles exceeds to 100 μm . It makes possible, in this case, to perform the micro-characterization on single micro-particles, such as micro Raman spectrum and electron probing micro-analysis. Subsequently, the high quality MgCO_3 single crystal growth could be attempted in the further by controlling the temperature, the pressure, the reaction time, the cooling rate and other experimental conditions [19].

Fig. 5 shows the TG and DSC analysis of as-synthesized MgCO_3 at the heating rate of 5 $^\circ\text{C}/\text{min}$ in argon atmosphere. A sharp weight reduction at around 500 $^\circ\text{C}$ was indicated from the TG curve, whereas a strong endothermic peak is observed obviously from DSC and the quantity of endothermic disintegration Q can be calculated as follows:

$$Q = \int_{400^\circ\text{C}}^{600^\circ\text{C}} \text{DSC}(t) dt = 128.59 \text{ kJ/mol}$$

The value of TG at 400 $^\circ\text{C}$ is 99.4%, which caused by a little absorbed water (<1%) on the surface of MgCO_3 sample. Because actually a large number of magnesite can lie stably in the nature, MgCO_3 sample can keep purity for quite a long time even without any drying protective agent and not react with the water in the air. In this case, there is almost no difference between MgCO_3 and other carbonates, such as CaCO_3 , SrCO_3 , and BaCO_3 . Hence, anhydrous magnesium carbonate can be a lot used as a stable material. Based on the decomposed process, it is understanding that MgCO_3 could be a candidate of the best flame retardant material because of its proper decomposed temperature, chemical stability, lots of absorption of heat and lots of CO_2 releasing.

It is observed clearly from Fig. 6(a) that the (104) diffraction peaks shift to low angle while heating from 25 $^\circ\text{C}$ to 400 $^\circ\text{C}$. The unit cell parameters (a, c, unit cell volume) are give in Table 1 and shown in Fig. 6(b) (c). Many enough data points were collected from high temperature XRD to ensure an accurate and reasonable

result. The unit cell parameters show a linear and continuous increase with increasing temperature, and the linear relationship can be fitted as follows,

$$a(t) = 4.633 \left(1 + 4.632 \times 10^{-6} t \right),$$

$$c(t) = 15.0157 \left(1 + 1.639 \times 10^{-5} t \right)$$

$$V \text{ unit cell}(t) = 279.13 \left(1 + 2.576 \times 10^{-5} t \right)$$

The calculation of axial thermal expansivity exhibits an obvious anisotropy and indicates that the thermal expansion coefficient along c-axis ($\alpha_c = 1.639 \times 10^{-5} / ^\circ\text{C}$) is over three times more than the a-axis ($\alpha_a = 4.632 \times 10^{-6} / ^\circ\text{C}$), and the anisotropy is agreement with the previous studies on the nature magnesite [20,21]. The volume thermal expansion coefficient is also calculated with $\alpha_v = 2.576 \times 10^{-5} / ^\circ\text{C}$. The value of thermal expansion coefficient we obtained is smaller than the results of the nature magnesite reported before (Table 2), and this difference could be caused by Mn^{2+} , Fe^{2+} and Ca^{2+} impurities due to much larger cation radii.

4. Conclusion

A new synthesis and processing method has been devised to produce anhydrous magnesium carbonate successfully by a simple dehydration reaction under high pressure, and it could be a candidate of the best flame retardant material. Compared to the previous studies, the crystallinity quality is greatly improved with the micro-particle size exceeding to 100 μm , and this significant breakthrough could provide bases for MgCO_3 single crystal growth. The high temperature and high pressure research, including P-V-T equation of state and high pressure Raman spectroscopy, on high quality and high purity MgCO_3 samples can be carried out in the future.

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Appendix A. Supplementary data

Supplementary data related to this article can be found at <http://dx.doi.org/10.1016/j.jallcom.2017.01.258>.

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