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Synthesis of Lithium Metasilicate Powders at Low Temperature via Mechanical Milling

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The Li_2SiO_3 powder has been successfully synthesized at low temperature via mechanical milling process. By using $LiOH{\cdot}H_2O$ and tetraethyl orthosilicate (TEOS) as raw materials, Li_2SiO_3 powder with grain size of about 100 nm could be obtained at room temperature (~20°C) after mechanical milling for 120 h. This nano Li_2SiO_3 powder shows excellent thermal stability that no decomposing reaction or phase change would happen even after calcined at 900°C for 4 h. Experiments show that high concentration of the raw materials is helpful to the forming of Li_2SiO_3 phase. When the concentration of the raw materials is too low, no Li_2SiO_3 phase could be obtained. The investigation also shows that small content of B_2O_3 could accelerate the densifying speed of Li_2SiO_3 ceramics and decrease the thermal stability of Li_2SiO_3 phase.

I. Introduction

In recent years, Li_2SiO_3 has attracted significant attention due to its special performance in several fields. For example, Li_2SiO_3 is strongly considered as a kind of breeder material [1–3] which could be applied in the fusion reactor because of its good tritium solubility, thermo-physical, physical and chemical stability at high temperature.[4–7] It is also a potential fast-ion conductor material since [SiO_4] tetrahedral structure is found in lithium metasilicate.[8,9] Furthermore, it can be used for CO_2 captures due to its fine sorption effect for CO_2.[10,11]

Up to now, many different processes, such as solid-state reaction, precipitation,[5] modified combustion[2,4] and sol-gel,[10–13] have been successfully applied to synthesize Li_2SiO_3. Solid-state reaction process is the simplest way to prepare Li_2SiO_3 powder by calcining the mechanical mixture of silica and a lithium compound. However, this simplest process has some serious shortcomings including high calcination temperatures (700°C–1000°C), low purity, and serious aggregation of the product. To overcome these drawbacks, wet chemical processes, especially the combustion and sol-gel processes, have been widely investigated in recent years. Cruz *et al.*[2] studied the effects of temperature on Li_2SiO_3 phase by modified combustion method using LiOH and H_2SiO_3 as precursor. They synthesized Li_2SiO_3 phase with a few impurities ($Li_2Si_2O_5$, SiO_2) at 450°C and pure Li_2SiO_3 at 650°C. Zhang *et al.* [10] obtained Li_2SiO_3 powder at 450°C via sol-gel process. Unfortunately, the thermal stability of this Li_2SiO_3 powder is not very good and it would completely transform to $Li_2Si_2O_5$ at higher temperature (900°C).

Recently, Zhang *et al.*[11] synthesized pure Li_2SiO_3 powder with high thermal stability at a very low temperature of 40°C via sol-gel route by using $C_2H_5{\cdot}OLi$ and tetraethyl orthosilicate (TEOS) as raw materials. This result suggests that by choosing suitable raw materials, Li_2SiO_3 powder might be obtained at lower temperatures. The reaction process of LiOH and TEOS could be described as follows:

$$5SiO(OC_2H_5)_4 + 12H_2O = 5SiO_2 + 12C_2H_5OH \tag{1}$$

$$2LiOH + SiO_2 = Li_2SiO_3 + H_2O. \tag{2}$$

As we know, the first step (reaction 1) could be finished under room temperature very easily, so the whole reaction was controlled by the second step (reaction 2). According to the law of thermodynamics, for any reaction:

$$\Delta G^{\theta}_{R,T} = \Delta H^{\theta}_{R,298\mathrm{K}} - T\Delta S_{R,T}. \tag{3}$$

$G^{\theta}{}_{R,T}$: standard Gibbs free energy of formation; $H^{\theta}{}_{R}$: standard enthalpy; $\Delta S_{R,T}$: entropy change. H, T, and S are state functions.

According to a specified formula (3) and thermodynamical data (Table I), the Gibbs free energy of the reaction (2) were calculated: $\Delta G^{\theta}{}_{R,25°C} = -54.96<0$. This result indicates that the reaction can occur spontaneously at room temperature.

On the basis of the calculation result, the objective of the present work is to synthesis pure Li_2SiO_3 powders at a very low temperature (~20°C) via mechanical milling using LiOH and TEOS as precursor. The factors which would influence the reaction process such as temperature and milling time on the powder have also been investigated.

II. Experimental Procedure

(1) Material Preparation

Lithium hydroxide ($LiOH{\cdot}H_2O$) and tetraethyl orthosilicate (TEOS, $Si\text{-}(OC_2H_5)_4$) were selected as starting materials. Stoichiometric proportions of the above raw materials with different concentrations were mixed in distilled water medium using zirconia balls as milling media at room temperature (~20°C) for 12, 24, 72, and 120 h. The rpm of the devices we are using can reach 50 rpm/min. The concentrations are listed in the following table (Table II). After milling, the wet mixture was dried in air. The obtained powders were divided into three parts. One part was characterized directly. Another part was calcined at different temperatures to investigate the thermal stability. The third part that was milled for 120 h

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Table I. Thermodynamical Data

Substance	LiOH(s)	SiO_2(s)	Li_2SiO_3(s)	H_2O(s)
$\Delta H^{0}_{298K}/(\mathrm{KJ{\cdot}mol^{-1}})$	−487.5	−910.7	−1648.1	−285.8
$\Delta S_{R,T}/(\mathrm{J{\cdot}(mol{\cdot}°C)^{-1}})$	42.8	41.5	79.8	70

Table II. Concentration of The Raw Materials

Sample	$LiOH{\cdot}H_2O$ (*M*)	TEOS (*M*)	H_2O (g)
a	0.66	0.33	60
b	1.66	0.83	60
c	3.32	1.66	60
d	5.0	2.5	60

was mixed with 0–4 wt% B_2O_3 additions and remilled for 24 h. After drying and sieving, the powders were uniaxially pressed under a pressure of 100 MPa into disks measuring 16 mm in diameter and 3 mm in thickness. These pellets were sintered at temperatures of 700°C–900°C for 4 h in air with the heating rate of 2°C/min.

(2) Characterization Techniques

Using X-ray diffractometry (XRD) using an Advance Bruker D8 X-Ray Diffractometer (Bruker ADVANCE, Karlsruhe, Germany) with Cu*K*α radiation Li_2SiO_3 compounds were identified. The operating voltage and electric current were, respectively, 40 kV and 40 mA. Scans were recorded in the (2θ) range 10–80°with a scan rate of 12°/min. The morphology of the crystals constituting the various samples was studied using scanning electron microscopy (SEM) (JSM-6360LV, Tokyo, Japan). The materials were filmed on the pellets of KBr. Fourier-transform infrared (FT-IR) spectra were taken in the above dried pellets in the frequency range of 400–3500cm^{-1} using a Nicolet 5700 Fourier spectrophotometer (Waltham, MA). The densities of the powder were calculated according to the principle of Archimedes, using the following formula:

$$D_b = G_1/(G_3 - G_2) \times D_L \tag{4}$$

.

D_b: bulk density; G_1: dry weight; G_2: buoyant weight; G_3: saturated wet weight; D_L: density of the water, 1 g/cm^3.

III. Results and Discussion

Figure 1 shows the XRD patterns of Lithium metasilicate powders synthesized after milling for different times at about 20°C (sample d). The results of XRD show that the milling time has obvious influence on the synthesizing of the Li_2SiO_3 phase. After milling for 12 h, the peaks of Li_2SiO_3 phase has become the main phase in the mixture, but some other phase such as SiO_2 could still be detected which reveals that TEOS do not react completely with lithium hydroxide. As time increased to 120 h, no impurities could be detected and all raw materials were transformed to Li_2SiO_3. This result indicates that the reaction can occur spontaneously under room temperature, which was compatible with the calculation result given in the introduction. Here one important fact that should be pointed out is that both LiOH and TEOS are soluble and the reaction 2 was carried out in water instead of in solid state, which might be the real reason why the reaction could complete at such a low temperature in the point of view of reaction dynamics. The morphology of the sample after milling for 120 h is shown in Fig. 2. From Fig. 2 it could be found that the powder is composed of well dispersed spherical particles with size of ~ 100 nm.

The concentration of the raw materials has obvious influence on the phase of final powder. Figure 3 is the XRD

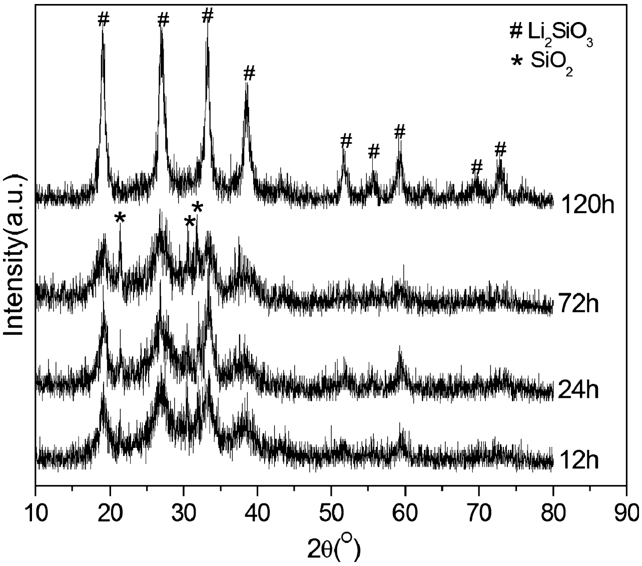

Fig. 1. XRD patterns of Li_2SiO_3 powders synthesized at about 20°C after milling different times.

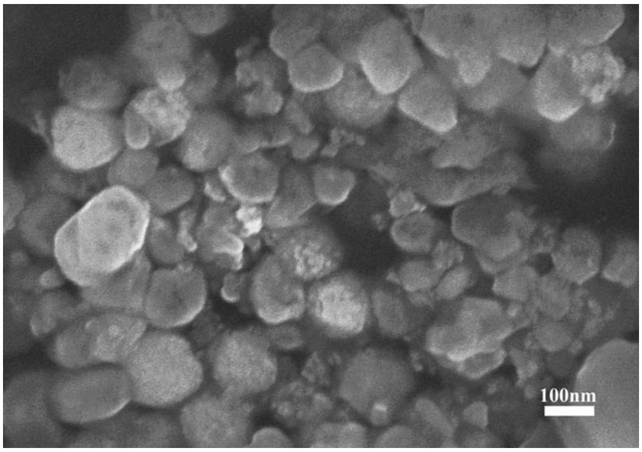

Fig. 2. SEM micrograph of Li_2SiO_3 powder synthesized at about 20°C after milling 120 h.

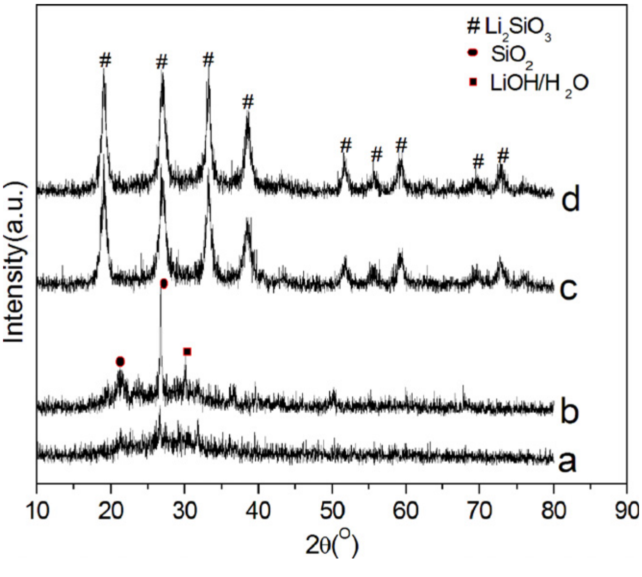

Fig. 3. XRD patterns of sample a–d milled at about 20°C for 120 h.

patterns of sample a–d after milled at about 20°C for 120 h. From Fig. 3 it could be found that when the concentration of $LiOH{\cdot}H_2O$ was 0.66 and 1.66 M (Sample a and Sample b), only some peaks of SiO_2 and $LiOH{\cdot}H_2O$ existed, and no Li_2SiO_3 phase could be detected. When the concentration of $LiOH{\cdot}H_2O$ increased to 3.32 M, Li_2SiO_3 became the main phase of the product accompanied by some other phases. Finally, when the concentration of $LiOH{\cdot}H_2O$ increased to 5.00 M, pure Li_2SiO_3 could be obtained. These results mean that the high concentration of the raw materials is helpful to the formation of the Li_2SiO_3 phase.

Figure 4 shows the XRD patterns of the powders (sample d) calcined at various temperatures. From Fig. 4 it could be found that when the temperature rose, the peaks of Li_2SiO_3 phase became higher and sharper, which means the structure of Li_2SiO_3 phase became integraler and the grain size became larger. Besides, no other impurity could be detected in the powder even when the temperature rose to as high as 900°C.

The FT-IR spectra of the powders calcined at various temperatures are shown in Fig. 5. The bands between 3550–3230 and 1647 cm^{-1} are assigned to O–H, which indicates that water existed in the powder when the temperature was ~ 20°C. The peak located at about 1439 cm^{-1} corresponds to the $–CH_2–$ band in $Si–OC_2H_5$. The absorption peaks between 1200–950 and 701–605 cm^{-1} are assigned to the asymmetric stretching vibration and symmetric stretching vibration of Si –O–Si, respectively. The bands between 850–550 cm^{-1} are due to vibration of O–Si–O and the bands between 530–400 cm^{-1} are due to the deformation vibrations of the terminal Si–O–(Li+) type bonds and Li–O vibrations [zhang]. The similar peak positions of the powders calcined at different temperatures indicated that molecular structures of the materials are stable and unaffected by heat treatment. This result, accompanied by the XRD patterns shown in Fig. 4, indicate that the thermal stability of the Li_2SiO_3 obtained by this simple mechanical milling at about 20°C was very good and could be a potential secure cathode material for application in the battery.

Figure 6 shows the densities of the Li_2SiO_3 material at different temperatures with and without B_2O_3-doped. The Li_2SiO_3 powders were obtained at 20°C for 120 h (sample d). As the sintering temperature rose, the density of the sample with no B_2O_3-doped kept increasing slowly. When the tem-

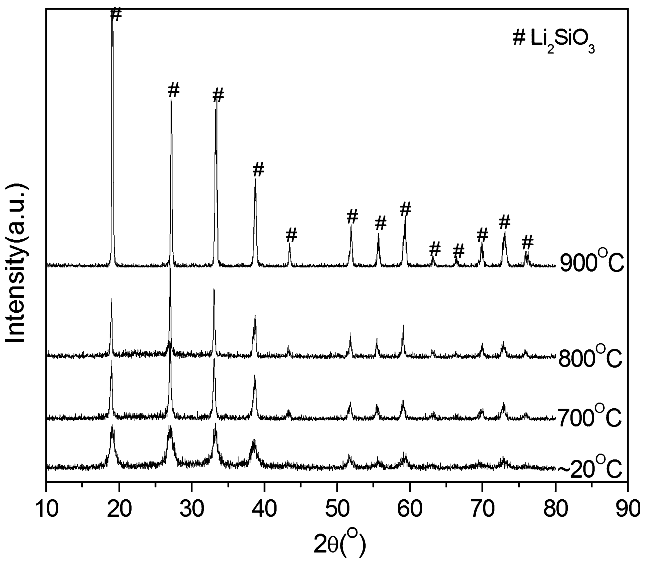

Fig. 4. XRD patterns of the powders calcined at various temperatures (sample d, milling 120 h).

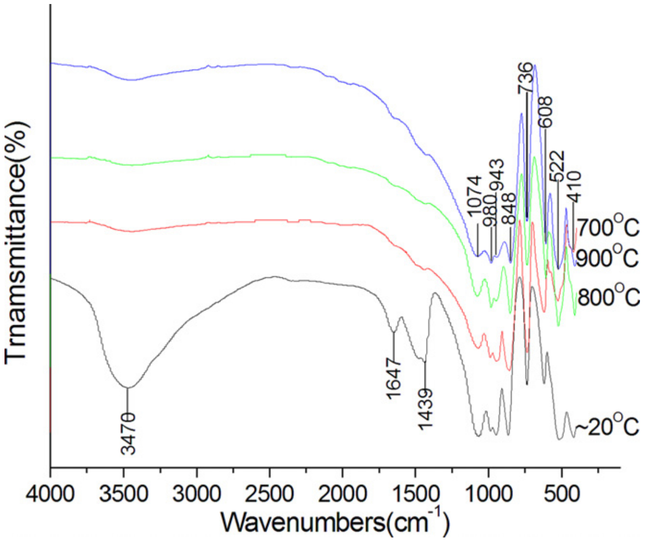

Fig. 5. Fourier-transform infrared spectra of the powders calcined at various temperatures (sample d).

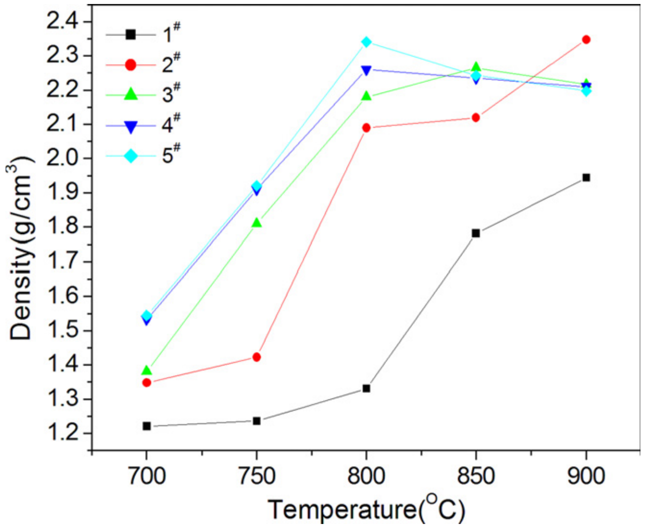

Fig. 6. Densities of the Li_2SiO_3 material sintered at different temperatures.

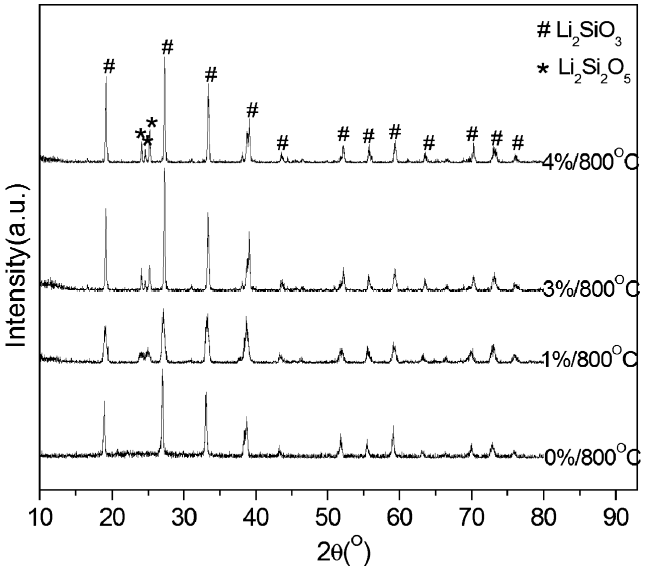

Fig. 7. X-ray diffraction patterns of Li_2SiO_3 ceramics with and without B_2O_3 added sintered at 800°C.

perature rose to 900°C, the density reached to ~ 1.9 g/cm^3. Then with small contents of B_2O_3 doping, the sintering temperature could be lowered to ~ 800°C and higher densities of ~ 2.3g/cm^3 could be obtained. These results suggest that B_2O_3 was effective to promote the sintering process.

Figure 7 shows the X-ray diffraction patterns of Li_2SiO_3 ceramics sintered at 800°C with and without B_2O_3 added. In Fig. 7 it could be found that different from the samples without B_2O_3 added, the peaks of $Li_2Si_2O_5$ phase could also be detected besides the Li_2SiO_3 phase in the B_2O_3 added samples. The more the B_2O_3 added, the higher the peaks of $Li_2Si_2O_5$ phase were. The intensity of $Li_2Si_2O_5$ phase peak increased as the increasing content of B_2O_3 added. This result means that the thermal stability of Li_2SiO_3 phase would decrease as B_2O_3 content increased.

IV. Conclusions

1. The forming of Li_2SiO_3 powder was influenced by milling time and concentration of raw materials. Longer milling time and higher concentration were beneficial for the forming of Li_2SiO_3 powder.
2. Li_2SiO_3 powder with particle size of ~ 100 nm was successfully synthesized at ~20°C via mechanical milling process.
3. The Li_2SiO_3 powder synthesized at ~ 20°C for 120 h shows excellent thermal stability that the crystal structure has no change even after being calcined at 900°C for 4 h.
4. Boron oxide ,B_2O_3 could effectively lower the sintering temperature and increase the densities of Li_2SiO_3 ceramics, but the thermal stability of Li_2SiO_3 decreased as the content of B_2O_3 was increased.

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