Synthesis and characterization of $NaAlSi_2O_6$ jadeite under 3.5 GPa*

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(Received 2 January 2017; revised manuscript received 16 February 2017; published online 20 April 2017)

The high pressure and high temperature (HPHT) method is successfully used to synthesize jadeite in a temperature range of 1000 °C–1400 °C under a pressure of 3.5 GPa. The initial raw materials are $Na_2SiO_3{\cdot}9H_2O$ and $Al_2(SiO_3)_3$. Through the HPHT method, the amorphous glass material is entirely converted into crystalline jadeite. We can obtain the good-quality jadeite by optimizing the reaction pressure and temperature. The measurements of x-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared (FTIR) and Raman scattering indicate that the properties of synthesized jadeite at 1260 °C under 3.5 GPa are extremely similar to those of the natural jadeite. What is more, the results will be valuable for understanding the formation process of natural jadeite. This work also reveals the mechanism for metamorphism of magma in the earth.

Keywords: synthetic jadeite, structural properties, HPHT

PACS: 82.75.Fq, 91.60.–x, 62.50.–p **DOI:** 10.1088/1674-1056/26/6/068202

1. Introduction

Jadeite is known as the king of the boulder. It is deeply favored by people as a kind of jewelry. In the ancient times, wearing jadeite was a symbol of identity and status. In addition, it possesses high collection value because natural jadeite is extremely rare. Jadeite is a kind of silicate rock and its main component is jadeite jade. The structural properties of the silicate melts are closely related to the physical, chemical, and thermal properties of magmatic liquids.[1–4] The collected information shows that these properties can explain the formation and evolution of magma in the earth, igneous processes and volcanism.[5,6] Furthermore, it is very important for us to understand the formation and deformation mechanism of silicate rocks. At the same time, the properties of synthetic jadeite are closely related to the formation of natural jadeite. Hence, one of the formation conditions of jadeite is high pressure.

At present, many techniques have been used to synthesize jadeite, such as the ultra-high pressure and high temperature polymerization method, the ion injection method and the high pressure and high temperature (HPHT) method, and so on.[7–9] However, it is quite difficult to obtain the ultra-high pressure and high temperature conditions and the cost of the ion injection method is extremely high. Hence, considerable attention has been paid to the method of HPHT. In 1948, Loring *et al*. synthesized the jadeite component of micro-crystalline powder in the first place.[10] In the 1960s, Bell and Kalb[11] and Hlabse and Kleppa[12] started to explore the best synthetic condition of the jadeite, and they suggested that the jadeite could be synthesized only under high pressure and high temperature conditions. In 1984, DeVries and Fleischer used amorphous glass powder, Al_2O_3, Na_2CO_3 and others as the initial raw materials to successfully synthesize jadeite samples with different colors by the ultra-high pressure and high temperature method for the first time.[13] In the 1990s, Zhao *et al*. used SiO_2, Al_2O_3, and Na_2CO_3 as the raw materials also to successfully synthesize the jadeite by HPHT method. But, the grain size and quality of their jadeite were not ideal.[14,15] In 2014, Wang *et al*. synthesized the jadeites under 5.0 GPa and the properties of synthetic jadeite quite resemble the natural jadeite on aspects in color, micro-structure and composition.[16] In 2015, Hu *et al*. synthesized the jadeites under 5.0 GPa–5.5 GPa and 1300 °C–1500 °C and the synthetic jadeite samples show highly saturated colors, are well crystallized and have good texture like those of the natural jadeite.[17] In the course of our experiments, we will study the synthesis and characterization of $NaAlSi_2O_6$ jadeite under 3.5 GPa.

In this study, we obtain a kind of ideal jadeite which is generated by optimizing the reaction pressure and temperature. After performing the tests of optical microscope, x-ray diffraction (XRD), scanning electron microscopy (SEM), Fourier-transform infrared (FTIR), and Raman scattering measurements, we find that the properties of synthesized jadeite

*Project supported by the National Natural Science Foundation of China (Grant Nos. 51172089 and 51171070) and the Graduate Innovation Fund of Jilin University, China (Grant No. 2016065).

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quite resemble those of the natural jadeite.

2. Experiments and methods

The selection of the initial raw materials has two main options: the one is SiO_2, Al_2O_3, and Na_2CO_3 and the other one is $Na_2SiO_3{\cdot}9H_2O$ and $Al_2(SiO_3)_3$. In this work, for the initial raw materials, we chose the high purity $Al_2(SiO_3)_3$ (99.99%) and Na_2SiO_3 (99.99%) powders. Then, a certain quantity of the raw materials were weighed according to the stoichiometry of $NaAlSi_2O_6$, and we mixed them sufficiently. Next, the powder of glass materials was obtained by quenching and grinding. In the end, the glass materials were shaped through a cold-pressing process. Experiments on jadeite crystallization were carried out in a China-type large cubic high-pressure apparatus (CHPA) (SPD-6 ×1200) with a sample assembly of 38 mm×38 mm×38 mm at a temperature range of 1000 °C–1400 °C under a pressure of 3.5 GPa. We obtained a series of the crystallographic samples by unloading the pressure and dropping the temperature.

Figure 1(a) shows the cavity structure of CHPA. In the experiments, the pressure is loaded through the moving of the six WC anvils together. The temperature is measured by using a Pt–Rh thermocouple (Pt RH/Pt Rh6 thermocouple) placed near the samples. The internal pressure and temperature calibration of the assembly have already been described in Ref. [18]. The schematic diagram of the experimental assembly for synthesizing jadeite samples is shown in Fig. 1(b).

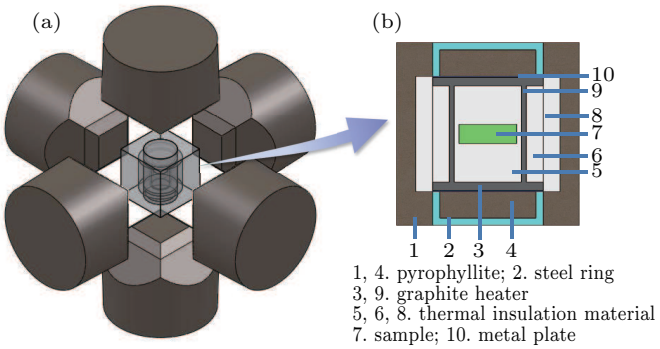


Fig. 1. (color online) (a) the cavity structure of CHPA and (b) the schematic of the experimental assembly.

The characterizations of synthesized samples were analyzed by the optical microscope, Raman spectra, infrared spectra, x-ray diffraction (XRD), and SEM micro-morphology. The x-ray diffraction measurements with the Cu-Kα (λ = 1.5418 Å) radiation were examined by an x-ray diffractometer (D/MAX-RA) and the infrared spectra were measured with the Perkin–Elmer 2000 FTIR spectra in a spectral range of 400 cm^{-1}–4000 cm^{-1} with a resolution of 2 cm^{-1} in transmittance mode.

3. Results and discussion

3.1. Phase analysis

Figures 2(a)–2(d) show the optical images of samples which are artificially synthesized at different temperatures under 3.5 GPa. As is well known, the natural jadeite possesses high quality in color and glossiness. However, some of the synthesized jadeite samples have different degrees of uneven coloring as shown in Figs. 2(a) and 2(b). But, the samples in Figs. 2(c) and 2(d) have better quality in color and luster than the samples in Figs. 2(a) and 2(b). Nevertheless, some cracks appear in the sample (see Fig. 2(d)), because the synthesis temperature is too high.

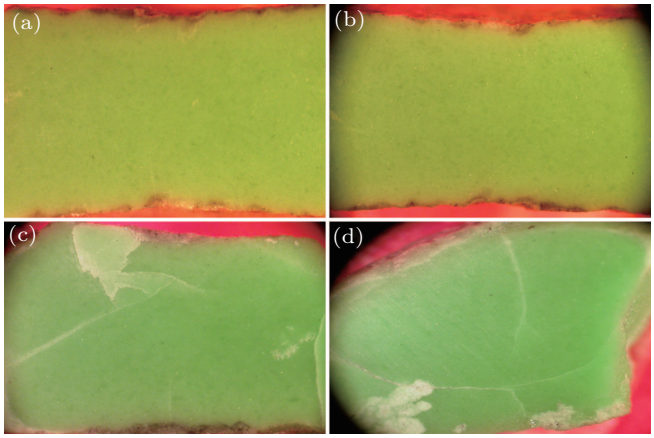


Fig. 2. (color online) Optical images of samples (a) synthesized at temperature 1140 °C and pressure 3.5 GPa, (b) at temperature 1200 °C and pressure 3.5 GPa, (c) at temperature 1260 °C and pressure 3.5 GPa, and (d) at temperature 1320 °C and pressure 3.5 GPa, respectively.

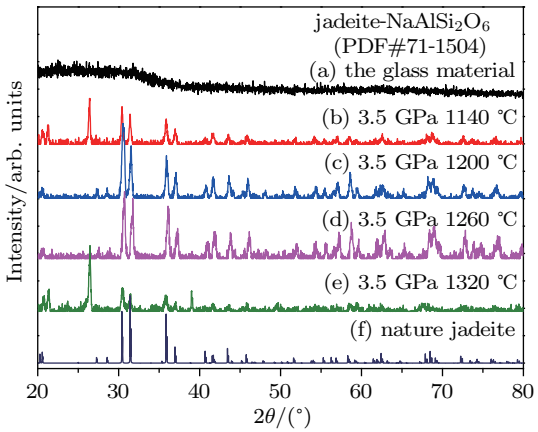


Fig. 3. (color online) XRD patterns of synthetic samples prepared by HPHT.

In order to analyze the composition of the synthetic jadeite, XRD is carried out to analyze the glass material powder and the synthesized jadeite samples by HPHT method, and the results are shown in Fig. 3.[19] We can see that the glass material shows the amorphous phase, because there appears no obvious diffraction peak in Fig. 3(a). Furthermore, the samples in Figs. 2(b) and 2(e) both present impurity phases, implying that they are quartz. However, comparing the XRD patterns in Figs. 3(c) and 3(d) with those of the natural jadeite

(f) (PDF#71-1504), we find that the diffraction pattern shows that they are entirely converted into jadeite. Hence, the main components of the samples in Figs. 3(c) and 3(d) are both $NaAlSi_2O_6$.

3.2. Micro-structure

In addition, the samples can also be analyzed in combination with scanning electron microscopy (SEM). The microstructures of the glass material, the synthetic jadeite and natural jadeite are clearly illustrated in Figs. 4(a)–4(f). According to what we have known, the micro-structure of natural jadeite is highly ordered and has an interpenetrating fibrous texture as shown in Fig. 4(f). By comparing with Fig. 4(f), we find that the glass material in Fig. 4(a) has no obvious fibrous texture, so it is of the amorphous phase. In addition, with temperature increasing, the arrangement changes into a more ordered one, and the structure became of a more interpenetrating fibrous texture as shown in Figs. 4(b)–4(d). The fibrous texture of the sample has been described by Carpenter and Bradt.[20,21]

In Fig. 4(d), the micro-structure of the sample resembles that of the natural jadeite especially, because the sample in Fig. 4(d) and the natural jadeite both have similar fibrous textures. But, the fibrous grains of the sample in Fig. 4(d) are thicker than the natural jadeite's. However, in Fig. 4(e), we can see that the arrangement cannot be kept in order and compact when the temperature is too high. At the same time, the fibrous grains become bigger than those of the natural jadeite. It is confirmed that the temperature plays a significant role in forming the fibrous texture structure for the synthetic jadeite sample.

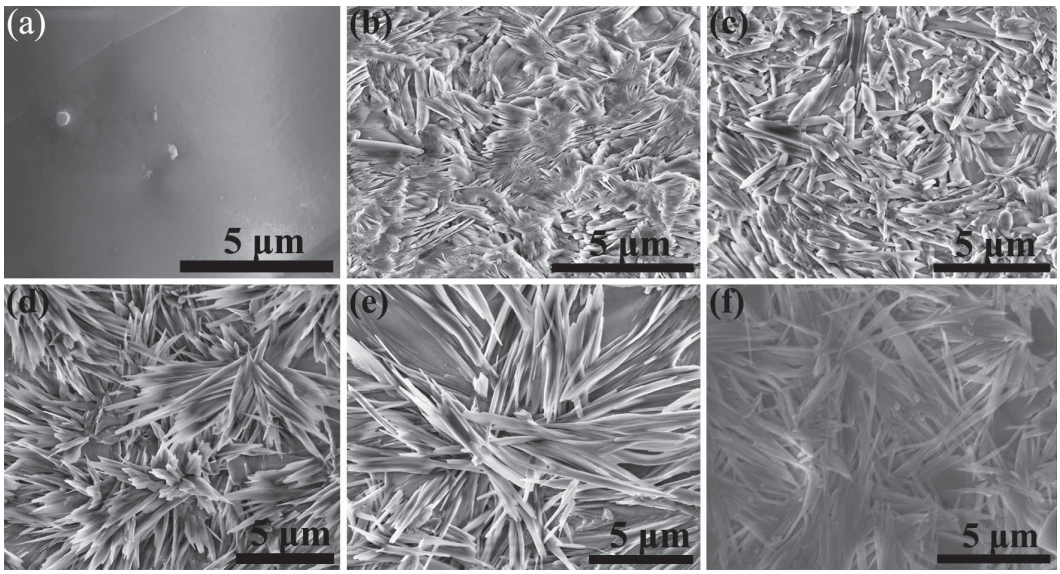


Fig. 4. SEM images of samples (a) of the glass material, (b) synthesized at temperature 1140 °C and pressure 3.5 GPa, (c) synthesized at temperature 1200 °C and pressure 3.5 GPa, (d) obtained at temperature 1260 °C and pressure 3.5 GPa, (e) obtained at temperature 1320 °C and pressure 3.5 GPa and (f) natural jadeite.

3.3. Raman spectra

It is well known that jadeite is a type of chain silicate: the two vertex angles of each silicon oxygen tetrahedron connect the adjacent oxygen-silicon tetrahedron with a chain of unlimited extension. The different chains are connected through the metal cations Na^+ and Al^{3+}. The characteristic peaks of Raman spectrum of the natural jadeite are closely related to the covalent chain of silicon oxygen tetrahedron. Figure 5 shows the Raman spectra of the jadeite synthesized under 3.5 GPa at different temperatures and the natural jadeite in a range from 100 cm^{-1} to 1100 cm^{-1}.

Figure 5(a) shows that the glass material does not have obvious characteristic peaks, indicating the amorphous phase. In contrast, the natural jadeite of Fig. 5(f) has some characteristic peaks, such as $\sim$ 204 cm^{-1}, $\sim$ 378 cm^{-1}, $\sim$ 702 cm^{-1}, and $\sim$ 1040 cm^{-1}. Meanwhile, we find that the synthetic jadeite contains the same characteristic peaks as the natural jadeite. The vibration bands at $\sim$ 372 cm^{-1} and $\sim$ 698 cm^{-1} can be attributed to the Si–O–Si bending vibration and are related to the covalent chain of silicon oxygen tetrahedron.

The vibration leads to the appearance of the peak of $\sim$ 1037 cm^{-1}. The other vibration frequency bands are found to be due to the M–O stretching vibration, the Si–O bending and coupled vibration. The M denotes the metal cations Na^+ and Al^{3+}. Comparing the three strongest peaks of Raman spectra of the sample (d) with the natural jadeite's, the slight deviation can be found. The phenomenon may be caused by the residual stress in the crystal. The results demonstrate that the crystal structure of the sample at 1260 °C under 3.5 GPa is the same as the natural jadeite's.[22,23]

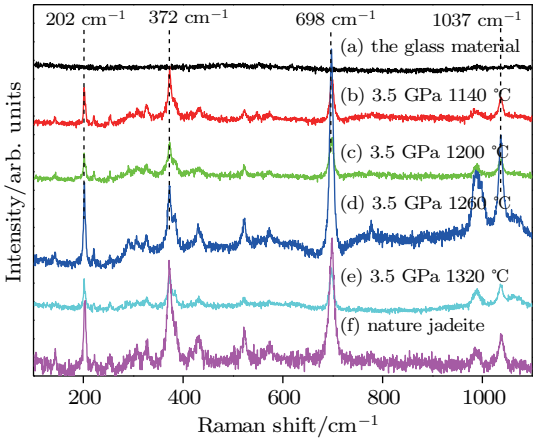


Fig. 5. (color online) Raman spectra of synthetic samples by HPHT.

3.4. Infrared spectra

Figure 6 shows the FTIR spectra of synthetic jadeite at 1260 °C under 3.5 GPa and natural jadeite in a range from 400 cm^{-1} to 2000 cm^{-1}. The main absorption peaks at ~ 919 cm^{-1}, ~ 992 cm^{-1}, and ~ 1056 cm^{-1} in a range from 900 cm^{-1} ~ 1100 cm^{-1} are caused by the Si–O vibration bond. The two vibration frequency bonds (~ 661 and ~ 744 cm^{-1}) at 600 cm^{-1}–800 cm^{-1} can be attributed to Si–O–Al vibration band and the Si–O bending vibration. The occurrence of vibration frequency bands (~ 436, ~ 464, ~ 494, and ~ 591 cm^{-1}) is due to the M–O stretching vibration, the Si–O bending and coupled vibration, respectively.[24] The M takes the place of the metal cation Na^+ and Al^{3+}.

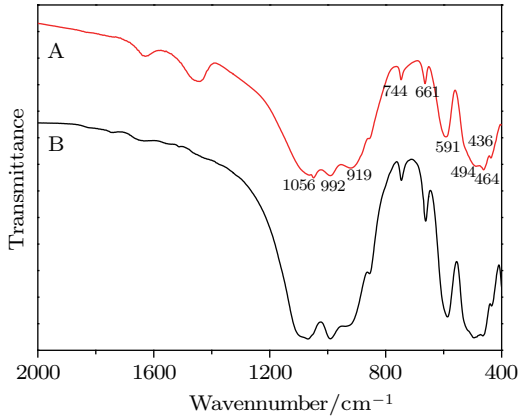


Fig. 6. (color online) FTIR spectra of synthetic sample A at 1260 °C under 3.5 GPa and sample B the natural jadeite.

The infrared absorption spectrum of the synthetic sample at 1260 °C under 3.5 GPa has the characteristic peaks which are like the natural jadeite's. However, the strongest band of the natural jadeite appears at ~ 1069 cm^{-1}. But, compared with the strongest peak of the natural jadeite, the strongest peak of the synthetic sample has a slight deviation. The phenomenon may be caused by the impurity elements replacing aluminum ion in crystal. The result also reveals that the crystal structure of sample A is quite similar to the natural jadeite's crystal structure.

4. Conclusions

In this study, the jadeites are successfully synthesized at 3.5 GPa and different temperatures by using the HPHT method and the main components of the synthetic jadeite samples are all $NaAlSi_2O_6$. It is confirmed that the temperature plays a significant role in forming the fibrous texture structure. The characterizations of synthetic jadeite at 1260 °C under 3.5 GPa are consistent with those of the natural jadeite in terms of the color, degree of crystallinity, fibrous texture structure, etc. The results will be helpful for us to in depth understand the formation mechanism of natural jadeite and the metamorphism of magma in the earth.

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