Synthesis of transparent polycrystalline jadeite under high pressure and temperature

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Attempts to synthesize transparent polycrystalline jadeite have been made by direct conversion from bulk glass at pressures 10–20 GPa and temperatures 900–1300 °C using Kawai-type multianvil apparatus. The grain size of jadeite tends to decrease with increasing pressure, but we failed to synthesize polycrystalline jadeite with grain sizes in nano-regime (<100 nm) and obtained the sample with the smallest average grain size of ~ 240 nm at 20 GPa and 1300 °C for 20 min. Polycrystalline jadeite of the minimum grain size exhibits high optical transparency with a transmittance of ~ 70% for a typical wavelength in the visible region. The highest Vickers hardness (Hv) of 14.2 GPa was observed for the polycrystalline jadeite sample with the minimum grain size of ~240 nm, which is about 7% higher than the hardness (Hv = 13.3 GPa) of the sample with the largest grain size of ~ 390 nm. Further increases in optical transparency and hardness of polycrystalline jadeite would be realized if we get nano-polycrystalline samples by optimizing pressure, temperature, heating duration, etc. of the ultra-high-pressure synthesis experiment.

Keywords: Jadeite, Transparent ceramics, Nano-polycrystal, Ultra-high-pressure synthesis

INTRODUCTION

Jadeite, having the end-member composition of NaAlSi2O6, is commonly formed in metamorphic rocks under high pressure and at low temperature, such as associated with subduction of crustal/sedimentary materials. Jadeite is also an important member of pyroxene in the mantle, which is the second most abundant mineral after olivine in ultramafic rocks of the upper mantle origin. Experimental studies demonstrate that NaAlSi2O6 jadeite is formed from an assembly of NaAlSi3O8 albite + NaAlSiO4 nepheline at pressures above ~ 2 GPa (Bell and Roseboom, 1969) and is stable up to ~ 22 GPa (Liu, 1978; Akaogi et al., 2002), above which it decomposes into an assemblage of calcium ferrite-type NaAlSiO4 + SiO2 stishovite. It is also shown that pyroxene in subducted basaltic rocks becomes Na-rich upon the pyroxene–garnet transformation in the deeper region of the upper mantle, leading to the formation of jadeite–rich pyroxene under pressure and temperature conditions of the mantle transition region (Irifune et al., 1986; Gasparik, 1989).

On the other hand, natural jadeite is known as a gemstone because of its characteristic greenish appearance and high wear resistance and selected as the national stone of Japan in 2016 by Japan Association of Mineralogical Sciences (Tsuchiyama, 2017). Natural jadeite is a polycrystalline mineral and exhibits low transparency for visible light, which is caused by scattering of the light at grain boundaries due to birefringence of this mineral with a monoclinic crystallographic structure. Natural polycrystalline jadeite also has notably high fracture toughness (Kic ~ 7 MPa m1/2; Bradt et al., 1973), which is attributed to its peculiar whisker structure with acicular micro-crystals.

Ceramics, made of oxides, nitrides, carbides, and silicates, including polycrystalline jadeite, generally show low optical transparency because of scattering of light by internal pores and grain boundaries. Recent developments in sintering techniques at low pressures (<1 GPa) succeeded to reduce the amount and the size of the pores substantially, leading to highly transparent ceramics, re-
ferred to as ‘transparent ceramics’ (e.g., Frange et al., 2007). Some of such transparent ceramics have been commercially applied to optical windows, scintillator, laser materials, etc. (e.g., Ikesue and Yan, 2008; Kameshima et al., 2019). However, these sintering techniques inevitably induce significant grain growth, and the grain sizes of such transparent ceramics are generally far greater than those in nano-regime (<100 nm). Transparent ceramics with grain sizes much smaller than those of the wavelength of visible light (~ 400–800 nm) were expected to have high optical transparency and excellent mechanical properties relative to those of conventional transparent ceramics (Apetz and van Bruggen, 2003; Wollmershauser et al., 2014), although synthesis of such ‘transparent nanoceramics’ had been very challenging.

Irifune et al. (2003) firstly succeeded in synthesizing highly transparent nano-polycrystalline diamond, which was found to be harder than single crystal diamond, by direct conversion from graphite at pressures higher than 15 GPa and at temperatures above 2300 °C in Kawai-type multianvil apparatus (hereafter KMA). Nishiyama et al. (2012) subsequently synthesized nano-polycrystalline stishovite from bulk silica glass using similar ‘ultra-high-pressure’ (the term generally used for pressures above 10 GPa in materials science) synthesis technique at 15 GPa and at 1000 °C. It was shown that nano-polycrystalline stishovite had exceptionally high fracture toughness, in addition to its very high hardness, but showed only low transparency in spite of its small grain size of ~ 100 nm, presumably due to the high maximum birefringence of stishovite (i.e., the difference between the maximum and minimum refractive index, Δn = 0.027; Stishov and Popova, 1961). More recently, Irifune et al. (2016) reported synthesis of nano-polycrystalline garnet from bulk glass at pressures above 10 GPa and temperatures around 1400 °C, which exhibited very high optical transparency equivalent to that of a single crystal for visible light, and was about 30% harder than the corresponding single-crystal garnet. Furthermore, highly transparent nano-polycrystalline kyanite with a triclinic symmetry and low birefringence (i.e., Δn = 0.012–0.016; Kerrick, 1990) was also reported by direct conversion from glass at 10 GPa and 1200 °C (Gaida et al., 2018), although the kyanite sample in this study contained a certain amount (~ 8.6 vol%) of Al2O3 corundum due to a defect of SiO2 in the glass starting material relative to the stoichiometric composition.

The transparent nano-ceramics synthesized under such ultra-high-pressure conditions are made of minerals without birefringence (Δn = 0) for diamond and garnet, because of optically isotropic nature of these minerals with cubic crystallographic symmetry, or with low birefringence for kyanite, while nano-ceramics made of stishovite with quite high birefringence show rather low optical transparency, as the grain boundary scattering largely depends on birefringence in addition to the grain size for pore-free ceramics (e.g., Apetz and Bruggen, 2003).

In this study, we attempted to synthesize nano-polycrystalline jadeite, which has a relatively low birefringence (Δn = 0.012; Wolfe, 1955) compared to those of many other non-cubic minerals, at various pressures and temperatures using KMA. The effect of pressure, temperature, and heating duration on grain size was studied to synthesize transparent polycrystalline jadeite with smaller grain sizes in the nano-regime. Optical transparency and hardness of polycrystalline jadeite were evaluated for some of the synthesized samples without major visible micro-cracks.

**EXPERIMENTAL METHOD**

Starting material with a composition of NaAlSi2O6 was prepared from a mixture of Na2CO3, Al2O3, and SiO2 powders, which was pelletized, put into a platinum crucible, melted at 1600 °C for 23 h in an oven, and quenched under air. The recovered bulk glass was cored by an ultrasonic machining tool to form rods with a diameter of 4.5 mm and a thickness of 2 mm for the runs at 10 and 15 GPa, and also those with a diameter of 2.2 mm and a thickness of 2 mm for the runs at 20 GPa. The glass rod starting material was inserted in a gold capsule, which was placed in the furnace assembly as described in Figure 1.

High pressure and high temperature experiments were performed using the KMAs (ORANGE-2000 and ORANGE-3000) at Geodynamics Research Center, Ehime University. The second-stage WC anvils with dif-
ferent sizes for the truncated edge length (TEL) were used depending on target pressures; TEL = 11 mm for 10 and 15 GPa and TEL = 5 mm for 20 GPa. Pressure medium was a semi-sintered (Mg,Co)O octahedron with an edge length of 18 mm for TEL = 11 mm and that of 11 mm for TEL = 5 mm. We adopted two types of the furnace assembly; Pt foil was used as a heater with sleeves of LaCrO₃ for thermal insulator and of MgO for electric insulator in some earlier runs, while the LaCrO₃ sleeve was used as the heater in later runs for more stable heating. Run temperature was measured with a W₉₇Rₑ₃-W₇₅Rₑ₂₅ thermocouple, while the temperature was estimated from the power-temperature relation based on other runs with the same furnace assembly in a run (OS3385) where the thermocouple failure occurred upon compression.

Pressure was increased first to the target value over 4 h, and temperature was increased slowly to 800 °C in about 20 min for stable temperature generation and then raised to the target temperature in a few min. The temperature was maintained for 60 min, while a shorter heating duration of 20 min was adopted to suppress the grain growth in some additional runs at 20 GPa. Temperature was then decreased to about 600 °C within a few min, and pressure was decreased slowly over 3 h at this temperature for relaxation of stress in the sample to minimize the occurrence of cracks upon release of pressure. When the press load reached 0.5 MN, the temperature was decreased to the room temperature in 5-10 min while the press load was further decreased to ~ 0.2 MN.

Phase identification of the recovered sample was made based on X-ray diffraction measurement using a micro-diffactometer (Rigaku, RAPIDII) operated at a tube voltage of 40 kV and a current of 30 mA with the CuKα radiation beam collimated to ~ 100 μm. Microstructure observations and chemical composition analyses were made on mirror finished samples using a field emission scanning electron microscope (FE-SEM; JEOL, JSM-7000F) equipped with an energy-dispersive X-ray spectrometer (Oxford, X-max 20), where the measurements were conducted at a beam current of 1 nA and an accelerating voltage of 20 kV. We prepared thin foils of some of the recovered samples with thickness of 100-200 nm using a focused ion beam instrument (FIB; JEM-9310FIB), whose grain sizes were evaluated based on transmission electron microscope (TEM; JEOL, JEM-2010) observations. Grain size was measured by an intercept method (Mendelson, 1969) on more than 100 grains in the TEM images for all of the observed four samples.

Both sides of some of the recovered samples without major cracks were polished to a mirror finish with a thickness of 1.0 mm, and optical transmittance was measured using a spectrometer (JASCO, V-670) for a wave-length range from ultraviolet to visible light. The incident light beam with a diameter of ~ 1 mm was directed to the sample, and the transmitted light was detected by a photomultiplier tube with a scan speed of 1000 nm/min. for the wavelength. The transmittance data for 10 measurements were stacked to reduce the noise level.

Results and Discussion

Table 1 shows experimental conditions and identified phases in the run products, while the results of the measurements of grain sizes and hardness are also shown for some selected samples. Jadeite crystallized from the glass at temperatures around 1000 °C, and no other phases were observed in the present pressure and temperature conditions. The full width at half maximum of the 241 diffraction peak (the FWHM, hereafter) of synthesized jadeite, which does not overlap with any other peaks and locates at a higher diffraction angle, is also shown in Table 1 as an indicator of the relative grain size of jadeite. It should be noted that the peak broadness is actually related to the crystallite size rather than the grain size. However, it is hard to distinguish crystallites from grains in well-sintered polycrystalline materials, particularly in the nano-regime, and we use the term ‘grain size’ here equivalent to the crystallite size.

Figure 2 shows the X-ray diffraction profiles of the recovered samples synthesized at various temperatures at a pressure of 10 GPa for 60 min. Crystallization of jadeite was not observed at the lowest temperature of 900 °C, while the glass was mostly converted to jadeite at higher temperatures. The diffraction peaks at 1000 °C are sharper than those at 1100 °C (see also Table 1), suggesting the formation of jadeite with larger grain size due to the crystal growth that occurred just above the glass transition temperature located presumably slightly higher than 1000 °C at 10 GPa. The diffraction peaks became sharper again at 1200 °C (Fig. 2 and Table 1), as compared to those at 1100 °C, indicating that the grain sizes of jadeite are larger at 1200 °C due to grain growth at higher temperature. This tendency of variations of the grain size with temperature is also observed in the samples synthe-
sized at 15 and 20 GPa (Table 1) and is consistent with that observed in the crystallization of nano-polycrystalline grossular garnet from glass (Irifune et al., 2016).

Table 1. Experimental conditions and results

| Run No. | Press. (GPa) | Temp. (°C) | Time (min.) | Products | FWHM (deg.) | Grain size (nm) | Hv (GPa) |
|---------|-------------|------------|-------------|----------|-------------|-----------------|----------|
| OS3374  | 10          | 900        | 60          | Gl       | —           | —               | —        |
| OS3357  | "           | 1000       | “           | Jd       | 0.346       | —               | —        |
| OT2407  | “           | 1100       | “           | Jd       | 0.386       | —               | —        |
| OS3385  | “           | 1300*      | “           | Jd       | 0.327       | 393 (199)       | 13.3 (0.4) |
| OS3704  | 15          | 1000       | 60          | Gl (+Jd) | 0.348       | —               | —        |
| OS3463  | “           | 1100       | “           | Jd       | 0.498       | 267 (142)       | 13.3 (0.4) |
| OT2408  | “           | 1300       | “           | Jd       | 0.385       | —               | —        |
| OS3420  | 20          | 900        | 60          | Gl       | —           | —               | —        |
| OS3437  | “           | 1000       | “           | Gl (+Jd)** | —           | —               | —        |
| OS3482  | “           | 1100       | “           | Jd       | 0.419       | 252 (133)       | 13.6 (0.6) |
| OS3470  | “           | 1300       | “           | Jd       | 0.335       | —               | —        |
| OS3586  | 20          | 1100       | 20          | Gl (+Jd) | 0.329       | —               | —        |
| OS3593  | “           | 1200       | “           | Jd       | 0.337       | —               | —        |
| OS3600  | “           | 1300       | “           | Jd       | 0.390       | 238 (125)       | 14.2 (0.1) |

FWHM, full width at half maximum of the 241 diffraction peak of jadeite; Hv, Vickers hardness. * Temperature was estimated by the power-temperature relation. ** Proportion of jadeite was very small and determination of the FWHM was difficult. The numbers in parentheses are standard deviations in the measurements of grain size and Vickers hardness. Gl, glass; Jd, jadeite.

Figure 3 shows TEM images of the samples with relatively large FWHM values (~ 0.4–0.5), except for that of OS3385 (0.327; Table 1). It is seen that the jadeite crystals are in granular shapes, in contrast to common natural jadeite with the whisker micro-structures, and have average grain sizes of ~ 240–270 nm, while the latter sample synthesized at 10 GPa and 1300 °C has significantly larger average grain size of ~ 390 nm (Table 1).

Figure 4 depicts the phase relations for the NaAlSi2O6 composition and the results of the present study. The crystallization of jadeite occurs at temperatures around 1000 °C with a slightly positive pressure dependency. The minimum grain size of jadeite is realized at a temperature around 1100 °C, rather independent of pressure, considering the results of TEM observations and the FWHM measurements (Table 1). Jadeite with the largest average grain size (~ 390 nm) is observed at the lowest pressure of 10 GPa and at the highest temperature of 1300 °C, while that with the smallest grain size (~ 250 nm) is synthesized at the highest pressure of 20 GPa and at the modest temperature of 1100 °C. The pressure and temperature conditions for the average grain sizes of 300 and 400 nm are roughly illustrated by the dotted contours in Figure 4, based on the TEM observations and the FWHM measurements, taking the results of the dependence of the grain size on pressure and temperature for polycrystalline garnet with a more comprehensive data set (Irifune et al., 2016) into considerations. Although we did not determine the grain sizes of all of the jadeite samples by the TEM observations, it is most likely we were unable to synthe-
size the jadeite sample with grain sizes in nano-regime under these pressure and temperature conditions shown in Figure 4 for the heating duration of 60 min, in the light of the FWHM values.

In order to synthesize nano-polycrystalline jadeite, we made additional runs at 20 GPa and at 1100, 1200, and 1300 °C for a shorter heating duration of 20 min (Table 1) to suppress the grain growth. We found the sample with a high FWHM value synthesized at 1300 °C had the minimum average grain size of ~ 240 nm based on the TEM observations, but the grain size remained significantly larger than those in the nano-regime. As jadeite is known to break down into an assemblage of calcium ferrite-type NaAlSiO4 + stishovite at pressures around 22 GPa, we gave up synthesizing nano-polycrystalline jadeite in the present study. Further explorations by changing some key parameters, such as pressure, temperature, heating duration, and heating rate, are needed to synthesize real nano-polycrystalline jadeite with grain sizes less than 100 nm.

Some of the present polycrystalline jadeite samples are highly transparent, but most of the samples suffer major/minor cracks. Figure 5a shows the transmittance of light in the visible region for three samples with higher optical transparency and less cracks, whose grain sizes were determined by TEM observations. It is seen that the transmittance of the light decreases significantly with decreasing wavelength presumably due to grain boundary scattering.

Transmittance \( T \) of light in ceramics with a thickness of \( t \) can be evaluated by

\[
T = (1 - R_s) e^{-\gamma t}
\]

where \( R_s \) represents the surface reflection and \( \gamma \) is the scattering coefficient inside the sample. The scattering is caused by grain boundaries and pores, and accordingly \( \gamma \) is expressed as \( \gamma = \gamma_g + \gamma_p \). When ceramics having a porosity of \( p \) are made of spherical grains with a radius of \( d_g \) and pores with a radius of \( d_p \), the scattering coefficients of grain boundaries and pores for the light with a wavelength of \( \lambda \) are given respectively as follows (Apetz and Bruggen, 2003):
and where $\Delta n_\text{g}$ is the averaged birefringence and given by $2/3$ of the maximum birefringence ($\Delta n$) of the constituent crystal (Apetz and van Bruggen, 2003), while $\Delta n_p$ is the difference between the average refractive index (n) of the crystal and that of the air ($\Delta n_p = n - 1$).

Figure 5b shows the transmittance of the light with a specific wavelength of 645 nm, which is employed as a representative wavelength of the visible region in earlier studies (Apetz and van Bruggen, 2003; Gaida et al., 2018), in three polycrystalline samples shown in Figure 5a as a function of grain size. The theoretically predicted transmittance based on equations (1) and (2) is shown for polycrystalline jadeite ($\Delta n_\text{g} = 0.008$) assuming the porosity of the sample is zero and hence $\gamma_p = 0$ from equation (3), while the corresponding transmittances of polycrystalline samples of kyanite (+8.6 vol% corundum; $\Delta n_\text{g} = 0.013$, Gaida et al., 2018) and grossular garnet ($\Delta n_\text{g} = 0$) are also shown for comparison. The transmittances of the present samples are marginally consistent with the theoretically predicted curve for polycrystalline jadeite, and the highest transmittance of about 70% is realized for the sample with the smallest average grain size of ~240 nm.
the glass transition temperature, where the viscosity of the glass is greatly reduced. Study of the structural changes in glass with increasing pressure should be an important subject to understand the nucleation rate and nano-crystallization of the ceramics/minerals from glass under the ultrahigh-pressure regime, which is however beyond the scope of the present study. Nevertheless, we believe we can synthesize nano-polycrystalline jadeite with higher transparency by optimizing experimental conditions and procedures based on the present experimental results, which should lead to jadeite with much higher optical transparency and excellent mechanical durability.

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