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The physical and chemical properties of synthetic and natural jadeite for jewellery

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Jadeite was synthesized from its glass of stoichiometric composition $NaAlSi_2O_6$, and a colouring agent Cr_2O_3 (0.3–0.6 wt%) was added to achieve the emerald colour. The conditions employed were a pressure range of 3.0–5.0 GPa and a temperature range of 1150–1750 °C, for periods of 1–480 min. The physical and chemical properties of synthetic jadeite, such as microstructure, unit cell parameters, melting point, thermal stability, hardness, density and refractive index, etc., were compared with those of natural jadeite. The optimum crystallizing conditions for the synthesis of jadeite for jewellery were above 4.5 GPa, 1450 °C and 60 min. The synthetic jadeite was emerald in colour, translucent, 12 mm diameter and 6 mm thick.

1. Introduction

The family of jade minerals consists of nephrite and jadeite. The former $Ca_2(Mg, Fe)_5(Si_4O_{11})_2(OH)_2$, is derived from the alpine-type peridotite–dunite intrusives. The latter which belongs to a pyroxene of composition $NaAlSi_2O_6$ is the rarer mineral. Both minerals are well known as polycrystalline gemstones of great toughness and, potentially, of great beauty, but jadeite is harder than nephrite. Good quality jadeite is more highly prized and scarcer than nephrite.

According to geological investigation, jadeite is generally considered to be a high-pressure mineral. In the earth's crust, albite dissociates into two other phases, jadeite and quartz, or it combines with nepheline to form jadeite, in accordance with the following important mineralogical reactions

$$\underset{\text{albite}}{NaAlSi_3O_8} = \underset{\text{jadeite}}{NaAlSi_2O_6} + \underset{\text{quartz}}{SiO_2} \quad (1)$$

$$\underset{\text{albite}}{NaAlSi_3O_8} + \underset{\text{nepheline}}{NaAlSiO_4} = \underset{\text{jadeite}}{2NaAlSi_2O_6} \quad (2)$$

In petrology and geophysics, much interest in this mineral has been centred on the above two mineralogical reactions over the several past decades. Various thermodynamic aspects of one or both of these reactions were the subject of experimental work by Yoder [1, 2], Yoder and Weir [3], Kelley *et al.* [4], and Kracek *et al.* [5]. The *P–T* stability field of jadeite was calculated by Adams [6] on the basis of the above data, and determined by Bell and Roseboom [7], Robertson *et al.* [8], Newton and Kennedy [9], and Hlabse and Kleppa [10]. These mineralogical reactions have been studied directly by the high pressure–high temperature equilibrium approach, notably Reaction 1 by Birch and LeComte [11], Reaction 2 by Robertson *et al.* [8] and Newton and Smith [12]. The work of Birch and LeComte [11] was carried out in the temperature range 700–1100 °C, and under a pressure of 1.5–2.5 GPa. Essene *et al.* [13] indicated that jadeite might be formed under a pressure of 0.5–1.0 GPa and in the temperature range 150–300 °C. Other research has been done on the high-temperature crystal chemistry by Cameron *et al.* [14], and on the optical spectrum by Rossman [15] amongst others. These investigations have revealed the method of formation of jadeite in petrology, and showed that they indeed provide jadeite. However, the above synthetic jadeite cannot be used as jewellery. Because the maximum highest pressure and temperature of synthesizing jadeite can only be increased to 2.5 GPa and 1100 °C, it seems that these conditions were probably not high enough for it to form jewellery quality material.

Until the 1980s, jadeite as jewellery was synthesized using different techniques. It was first synthesized using a high-pressure technique by DeVries and Fleischer in 1984 [16], then it was synthesized by Suwa Seikosha Co. Ltd in 1985 [17]. In 1989, jadeite and fluorescent jadeite for jewellery were also synthesized using a Girdle press by Chen *et al.* [18] and Su *et al.* [19]: all of them obtained fine jadeite for jewellery.

The present work was intended to improve the experimental conditions in order to obtain good quality jadeite for jewellery. Jadeite was synthesized under a pressure of 3.0–5.0 GPa, and in the temperature range 1150–1750 °C, for periods of 1–480 min with a

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high-pressure apparatus for diamond synthesis – a cubic anvil press. The refinement of the crystal structure and the crystal transgranular fibrous texture state of both synthetic and natural jadeite were determined. Thermal stability of jadeite was studied at 1 atm by differential thermal analysis (DTA) and quenching experiments. Other physical and chemical properties of synthetic jadeite were also investigated by performing annealing and ageing experiments to check the stability of synthetic jadeite, as well as its hardness, density, index of refraction and composition, etc., in order to compare them with the properties of the natural jadeite.

2. Experimental procedure

The natural jadeite used here was bought from a jewellery store. It was translucent and green.

Jadeite was also synthesized by the following procedure. Upon melting Na_2CO_3 (99.9%), SiO_2 (99.0%), and Al_2O_3 (99.9%) in the proper proportions to make a stoichiometric composition of $NaAlSi_2O_6$, the resulting jadeite was obtained from a glassy phase at high pressure and high temperature. A small amount (0.3–0.6 wt %) of Cr_2O_3 (99.9%) was added as a principal colouring agent to obtain the typical green colour of jadeite. The above mixture was melted in a platinum crucible in air between 1350 and 1550 °C for 2–3 h. The molten liquid was quenched in cool water and the quenched glass was broken and crushed, and refired as many times as needed to produce a homogeneous product, because the viscosity of the liquid is very high even at 1350 °C (see, for example, Kushiro [20]). The quenched glass after homogenization was crushed to a 60–120 mesh powder and used in this form for conversion into jadeite by a crystallization process in its stability region. The powder was placed in a high-pressure cell with a graphite sleeve heater, as shown in Fig. 1. The cell and its contents were held at a varying pressure of 3.0–5.0. GPa, and a temperature of 1150–1750 °C in the stability region of jadeite for periods of 1–480 min. The temperature was then lowered to ambient conditions by shutting off the power to the cell; then the pressure was released, and jadeite was obtained.

In these experiments, the pressure was measured with the phase transformation of bismuth, thallium and barium under the known pressure (see Lloyd [21]). The temperature was measured with a 6% Rh Pt–30% Rh Pt thermocouple without correction for the effect of the pressure.

The unit cell parameters of the synthetic and natural jadeite were determined by powder X-ray diffraction. CuK_α radiation and a diffractometer scan rate of $1/2^\circ\ 2\theta\ min^{-1}$ were used with an internal standard of monocrystalline silicon. The unit cell parameters of clinopyroxene were calculated using 24 diffraction maxima in the range of 10°–60° 2 θ. Refinement of the crystal structure of the synthetic and natural jadeite was also investigated by scanning electron microscopy (SEM) and infrared absorption spectroscopy (IR) measured using a KBr disc and employing a PE 580E spectrophotometer at ambient conditions .

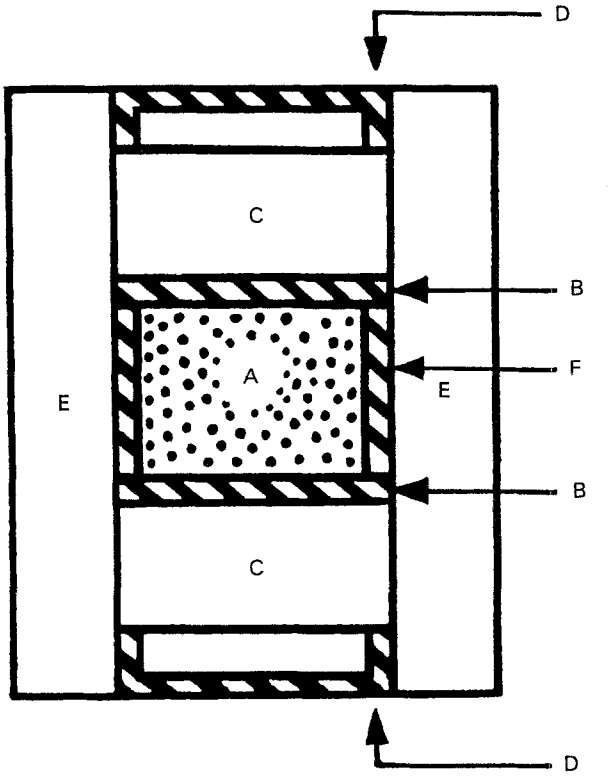

Figure 1 Schematic diagram of the high-pressure cell. A, sample area; B, graphite discs; C, bulk metal; D, electrode; E, insulation; F, graphite heater sleeve.

Annealing experiments were performed. The samples were put into an electric resistance furnace and heated to 500 °C in air, and held at this temperature for 15 h then annealed to ambient conditions. The increasing and decreasing temperature rates were both controlled to within 1 °C min^{-1}.

Quenching experiments were then carried out; the samples were put into an electric resistance furnace and heated to 800–1200 °C for 30 min or 24 h and then quenched to room temperature.

Samples were aged at 50 °C, and a relative humidity of 30%, light intensity about 180 klux, for 30 days (equivalent to 5 years under natural conditions).

3. Results and discussion

3.1. Microstructure of jadeite

The synthetic jadeite which was used for analyses of the refinement of the crystal structure was crystallized at 1450 °C and under 4.5 GPa for periods of 60 min.

3.1.1. Powder X-ray diffraction

Powder X-ray diffraction data and the unit cell parameters of the synthetic and natural jadeite are listed in Tables I and II. The powder X-ray diffraction data and unit cell parameters of synthetic jadeite are coincident with those of natural jadeite.

3.1.2. Scanning electron microscopy (SEM)

The fracture surfaces of the synthetic and natural jadeite were observed by SEM (see Fig. 2a and b). The

TABLE I X-ray powder diffraction data of synthetic and natural jadeite

HKL	*I*	d_{syn} (nm)	d_{nat} (nm)	*HKL*	*I*	d_{syn} (nm)	d_{nat} (nm)
110	11	0.6180	0.6196	112	25	0.2156	0.2158
020	29	0.4280	0.4281	022	25	0.2156	0.2151
−111	17	0.3340	0.3347	330	26	0.2065	0.2065
021	17	0.3240	0.3245	−331	26	0.2065	0.2066
220	21	0.3097	0.3098	−421	13	0.2041	0.2044
−221	100	0.2917	0.2917	041	21	0.1966	0.1966
310	86	0.2825	0.2825	−402	8	0.1991	0.1992
−311	86	0.2825	0.2827	202	6	0.1942	0.1941
−131	48	0.2484	0.2484	−132	9	0.1924	0.1926
002	48	0.2484	0.2480	510	12	0.1758	0.1757
221	34	0.2412	0.2414	150	10	0.1682	0.1682
311	18	0.2202	0.2202	−313	8	0.1651	0.1650

TABLE II Unit cell parameters of synthetic and natural jadeite

	a (nm)	*b* (nm)	*c* (nm)	β (°)	*V* (10^{-3} nm^3)
Synthetic jadeite	0.9439	0.8578	0.5233	107.28	404.2
Natural jadeite	0.9430	0.8574	0.5225	107.35	403.0

results reveal that they both have a similar texture, which is an interpenetrating fibrous crystal. This type of refined texture is the same as that described by Bradt *et al.* [22].

3.1.3. Infrared absorption spectra

Infrared absorption spectra of the synthetic and natural jadeite were measured under ambient conditions. Fig. 3a and b show the infrared absorptions between 1200 and 300 cm^{-1}. The vibration banks of Si–O stretching with the tetrahetra, Si–O terminal non-bridged stretching, O–Si–O bridged stretching between tetrahedra, and Si–O–Si, O–Si–O bending modes [23–27] are very similar between the synthetic and natural jadeite. The results also reveal that they both have a similar refinement of the crystal structure.

3.2. Macroquality of jadeite

3.2.1. Effect of pressure and temperature on macroquality

Jadeite was synthesized in the temperature range 1150–1750 °C, under a pressure of 3.0–5.0 GPa. for periods of 60 min, then surveyed and carved after the sample was polished. The observation results are listed in Tables III and IV.

3.2.2. Effect crystallization time on hardness

The samples were synthesized at 1450 °C, 4.5 GPa, for 1–240 min, and then the hardness was measured (see Fig. 4). When the samples were synthesized within 15 min, two kinds of hardness appeared at different

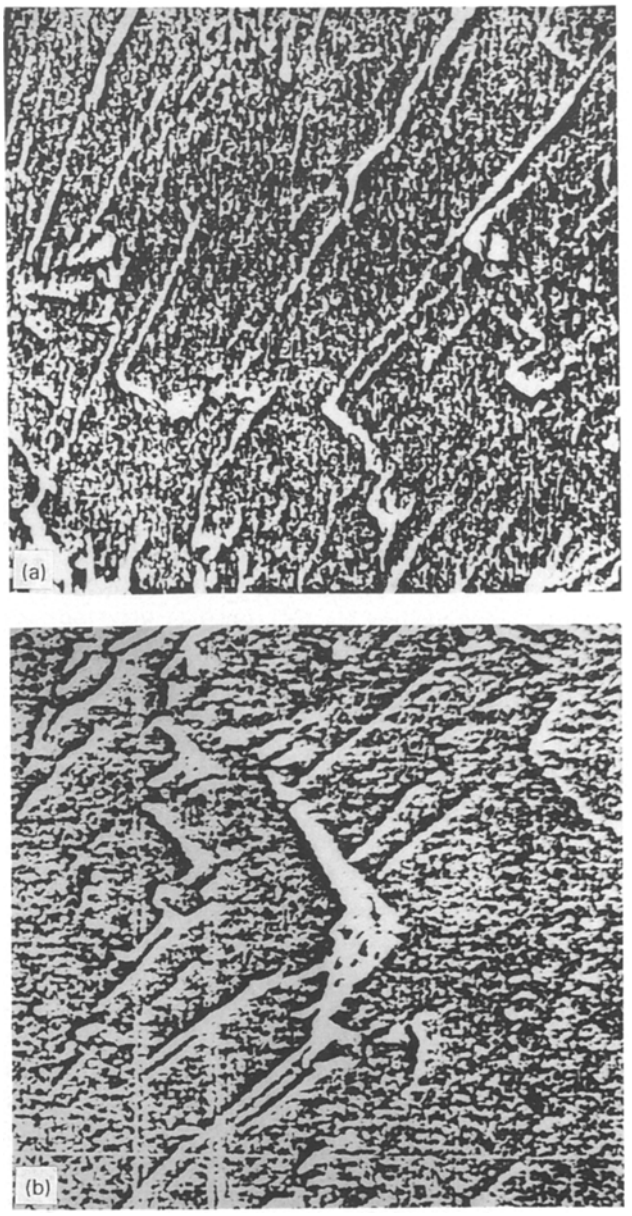

Figure 2 Scanning electron micrographs of the fracture surfaces of (a) synthetic and (b) natural jadeite. Note the interpenetrating fibrous texture. × 1200.

TABLE III Macroquality of samples synthesized in the temperature range 1150–1750 °C, under 4.5 GPa, for 60 min

Temperature	macroquality			
T (°C)	Colour	Quality	Transparency	Glossiness
1150	Light green	Loose	Opaque	No
1350	Green	Compact, hard	Opaque	Dark
1450	Emerald	Compact, fine, hard	Translucent	Bright
1550	Emerald	Compact, fine, hard	Translucent	Bright
1750	Emerald	Compact, fine, hard	Translucent	Bright

positions of the same piece of jadeite. This phenomenon reveals that the glass material is transformed into a heterogeneous structure of interpenetrating fibrous texture: the better the formation of the granular

TABLE IV Macroquality of samples synthesized under pressures of 3.0–5.0 GPa, and at a temperature of 1450 °C, for 60 min

Pressure	Macroquality			
P (GPa)	Colour	Quality	Transparency	Glossiness
3.0	Light green	Loose	Opaque	No
3.5	Green	Compact, hard	Opaque	Dark
4.0	Green	Compact, fine, hard	Opaque	Dark
4.5	Emerald	Compact, fine, hard	Translucent	Bright
5.0	Emerald	Compact, fine, hard	Translucent	Bright

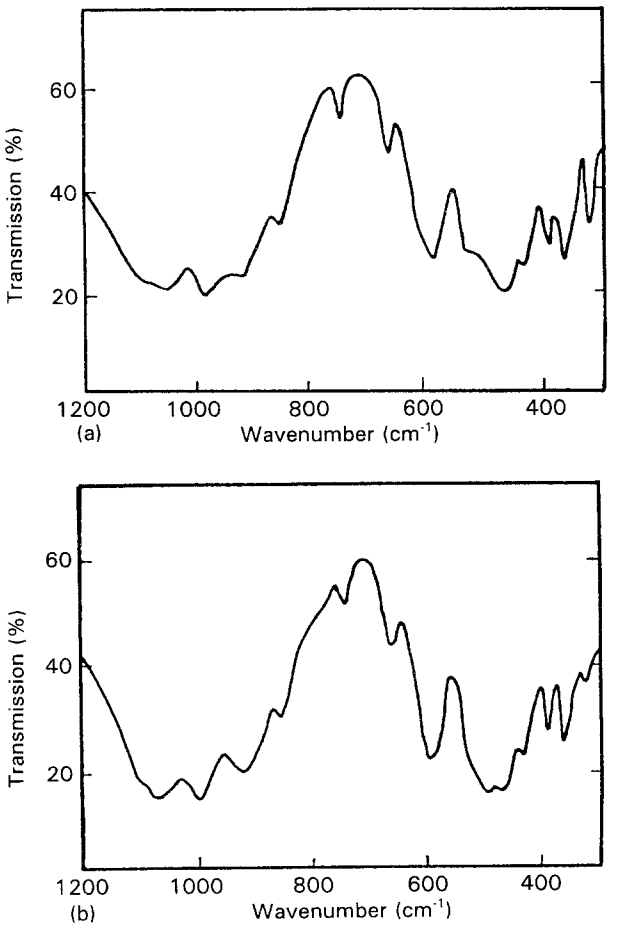

Figure 3 Infrared absorption spectrum of (a) synthetic and (b) natural jadeite.

fibrous structure in the same piece of jadeite, the higher is its hardness. On the contrary, the looser the formation of granular fibrous structure in the same piece of jadeite, the lower is its hardness. When the crystallization time is longer than 15 min, the hardness of synthetic jadeite, H_v, is over 1018 kgf mm^{-2} (translate into Mohs hardness above H6.8). The maximum hardness is 1088 kgf mm^{-2}. The hardness of the natural jadeite used in this work was H6.7. In general, the hardness of natural jadeite is reported to be in the range H6.5–7.0.

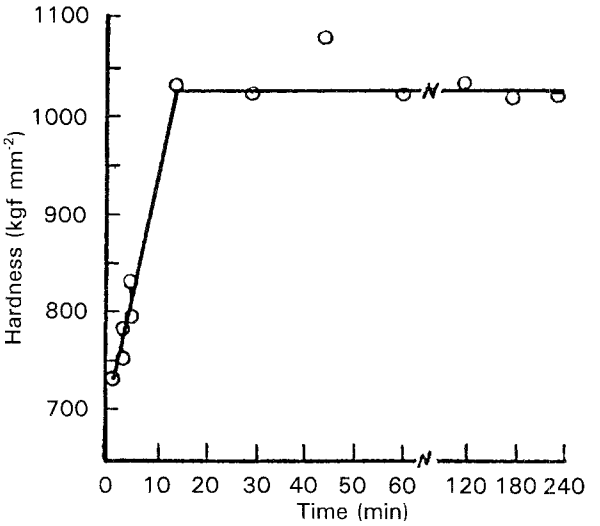

Figure 4 Variation of the hardness of synthetic jadeite with the crystallization time under 4.5 GPa and at 1450 °C.

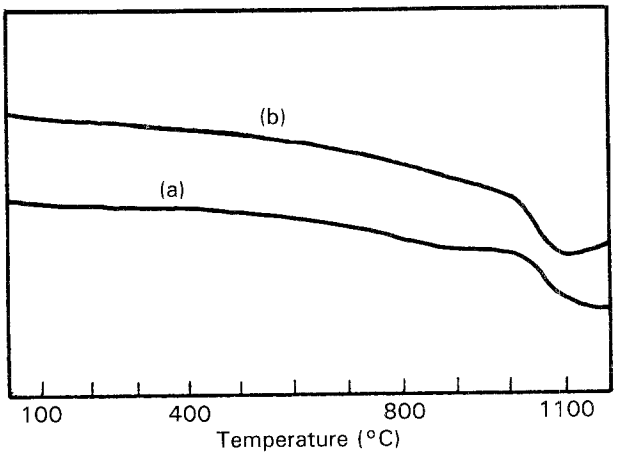

Figure 5 Differential thermal analyses of (a) synthetic and (b) natural jadeite at 1 atm in air; Heating rate, 10 °C min^{-1}.

3.2.3. Differential thermal analysis (DTA)

The DTA curves of both synthetic and natural jadeite indicate that they both have an apparent absorption of heat at nearly 1040 °C (see Fig. 5). This phenomenon reveals that a phase transformation takes place at this temperature. In fact, molten jadeite was discovered at this temperature. The melting point which has been measured for both synthetic and natural jadeite in our experiments is the same as that of the natural jadeite documented in the literature [28]. Therefore, the result implies that synthetic jadeite possesses the same thermal behaviour as natural jadeite.

3.2.4. Quenching of synthetic jadeite

The synthetic jadeite was heated at different temperatures and for different times, and then quenched to room temperature. The quenched samples were analysed by powder X-ray diffraction (see Figs 6 and 7). When the sample was kept at a temperature below the melting point for a short time (not longer than 30 min), the structure of the jadeite remained

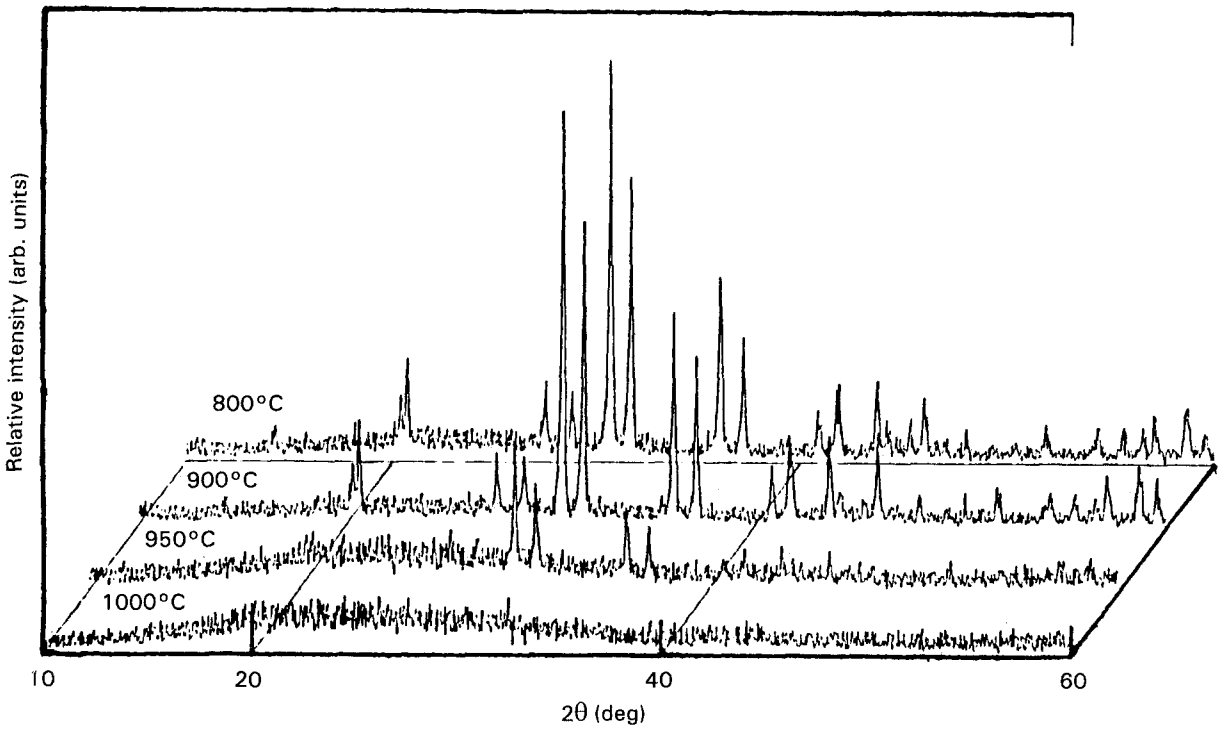

Figure 6 X-ray powder diffractographs of the samples quenched at high temperature. Soaking at high temperature for 30 min.

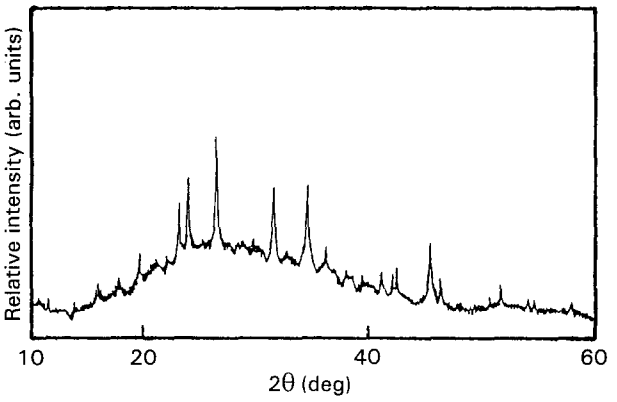

Figure 7 X-ray powder diffractograph of the sample soaked at 900 °C for 12 h and then quenched. The sharp peaks on the non-crystal background belong to those of nepheline.

unchanged. When the temperature exceeded the melting point, although the soaking time at this temperature was only 30 min, the jadeite was transformed completely into a glassy phase that was determined by powder X-ray diffraction experiments. When the soaking time was longer than 12 h, the jadeite was transformed into nepheline and albite (see Fig. 7) as in the following equation

$$2NaAlSi_2O_6 = NaAlSi_3O_8 + NaAlSiO_4 \quad (3)$$

jadeite nepheline albite

These phenomena suggest that jadeite is a metastable phase at 1 atm.

The quenching experiments showed that synthetic jadeite is molten at nearly 1000 °C. The DTA curves indicate that the phase transformation takes place at the temperature of 1040 °C. Both experimental results are in good agreement.

3.2.5. Annealing of synthetic jadeite

The samples were synthesized at 1450 °C and 4.5 GPa for 5–60 min, and then annealed. The colour of the jadeite was slightly changed after annealing. When the crystallization time was less than 30 min, the shorter the crystallizing time, the darker was the glossiness of the jadeite. White dots appeared on the surface of the samples, but the refined structure of jadeite, determined by powder X-ray diffraction, remained unchanged. However, when the crystallization time exceeded 30 min, no glossiness or colour change were found (see Table V).

The samples synthesized at 4.5 GPa in the temperature range 1150–1750 °C for 60 min were also annealed. When the crystallization temperature was lower than 1400 °C, white dots appeared on the jadeite surface while the microstructure, determined by powder X-ray diffraction, remained unchanged. However, when the crystallization temperature was higher than 1400 °C, the jadeite surface retained its primitive glossiness and colour after annealing (see Table V).

3.2.6. Ageing of synthetic jadeite

Samples which were crystallized in the temperature range 1150–1750 °C, and a pressure range of 3.0–5.0 GPa, for periods of 5–240 min were aged, and the results of these ageing experiments are listed in Table VI. The anti-ageing ability of the synthetic jadeite approached that of natural jadeite when the crystallization conditions exceeded 4.5 GPa, 1450 °C and 45 min. The texture, colour, and glossiness remained unchanged after an ageing experiment of 30 days (equivalent to 5 years under natural conditions). The surface of the synthetic jadeite was broken and produced a white substance when the crystallization

TABLE V Macroquality of the synthetic jadeite after annealing

Crystallization conditions			Macroquality			
P (GPa)	T (°C)	t (min)	Colour	Quality	Surface	Glossiness
4.5	1450	5	Slight change	Loose	White dots	Loss
4.5	1450	20	Slight change	Hard, compact	No dots	Slight loss
4.5	1450	30	No change	Hard, fine, compact	No dots	Bright
4.5	1150	40	Change	Loose	White dots	Loss
4.5	1350	60	Slight change	Loose	White dots	Loss
4.5	1450	60	No change	Hard, fine, compact	No dots	Bright
4.5	1750	60	No change	Hard, fine, compact	No dots	Bright translucent

TABLE VI Macroquality of the synthetic jadeite after ageing

Crystallization condition			Macroquality			
P (GPa)	T (°C)	t (min)	Colour	Quality	Surface	Glossiness
3.0	1450	60	Change	Cracked	Less $Na_2O + Na_2CO_3$	No
3.5	1300	120	Change	Cracked	$Na_2O_3 + Na_2CO_3$	No
4.0	1450	60	Green	Loose	No change	Dark
4.0	1750	30	Green	Compact, hard	No change	Bright
4.5	1350	30	Change	Cracked	$Na_2O + Na_2CO_3$	Loss
4.5	1450	45	Emerald	Hard, fine, compact	No change	Bright, translucent
5.0	1750	60	Emerald	Hard, fine, compact	No change	Bright, translucent

TABLE VII Density, refractive index, and hardness of synthetic and natural jadeite

	Density ($g\,cm^{-3}$)	Refractive index	Hardness, H
Synthetic jadeite	3.32	1.67	6.8
Natural jadeite	3.31	1.66	6.7
Average	3.24–3.43	1.66	6.5–7.0

TABLE VIII Compositions of synthetic and natural jadeite

	Na_2O	CaO	MgO	MnO	FeO, Fe_2O_3	Cr_2O_3	Al_2O_3	SiO_2
Theoretical value	15.34						25.21	59.45
Synthetic jadeite	16.33				0.55	0.49	23.48	59.03
Natural jadeite	12.75	1.67	1.22	0.51	0.48	0.92	22.73	59.62

of jadeite was carried out below the above conditions. The analysis results showed that this white substance consisted of Na_2O and Na_2CO_3.

3.2.7. Density and refractive index (RI)

Jadeite was synthesized at 1450 °C and 4.5 GPa for 60 min and then its density and RI were measured at 20 °C in air. The density of synthetic jadeite was 3.32 $g\,cm^{-3}$, and the RI was 1.67. The density and RI of the natural jadeite used here were 3.31 and 1.66, respectively (see Table VII). In general, the density and RI of natural jadeite are 3.24–3.43 and 1.66, respectively.

3.3. Composition analysis

The compositions of synthetic and natural jadeite (used in this experiment) were analysed using the inductively coupled plasma (ICP) method (see Table VIII). The composition of synthetic jadeite was found to be similar to that of natural jadeite.

4. Conclusions

1. The optimum conditions for synthesizing jadeite for jewellery were found to be a pressure range of 4.5–5.0 GPa, and a temperature range of 1450–1750 °C, for periods of 60–240 min.

2. Synthetic jadeite for jewellery is translucent and has an excellent emerald colour. It is also bright and glossy. Its physical and chemical properties are similar to those of natural jadeite.

3. The maximum size of synthetic jadeite obtained in our experiments for jewellery purposes is 12 mm diameter and 6 mm thick.

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