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Synthesis of the clinopyroxenes join $CaMgSi_2O_6$–$NaAlSi_2O_6$ for jewellery

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Clinopyroxenes of the join $CaMgSi_2O_6$(diopside)–$NaAlSi_2O_6$ (jadeite) were synthesized in the temperature range 800–1900 °C and under varying pressure, 10–55 kbar. The stability regions of various compositions of diopside–jadeite have been established experimentally using different compositions of glass materials: stoichiometric composition $NaAlSi_2O_6$, $0.1CaMgSi_2O_6$–$0.9NaAlSi_2O_6$, $0.2CaMgSi_2O_6$–$0.8NaAlSi_2O_6$, $0.3CaMgSi_2O_6$–$0.7NaAlSi_2O_6$, and $0.4CaMgSi_2O_6$–$0.6NaAlSi_2O_6$. Unit cell parameters of synthetic clinopyroxenes with the above compositions were determined. The physical properties, such as hardness, toughness, density, and refractive index, etc., were also measured. The results show that synthetic clinopyroxenes have the same properties as the natural one. The gem quality of diopside–jadeite clinopyroxenes was achieved by synthesised on the basis of the above experiments. Various colouring agents, such as Cr_2O_3, Co_2O_3, NiO_2, Fe_2O_3, TiO_2, MnO, CuO, and their combinations, FeO–Cr_2O_3, etc., were added to obtain the different colours of gem. In addition, small amounts of the rare-earth oxides, such as CeO_2, Nd_2O_3, Sm_2O_3, Dy_2O_3, Eu_2O_3, Er_2O_3, Pr_6O_{11}, Lu_2O_3 and CuO–Eu_2O_3, Co_2O_3–Nd_2O_3, etc., were also added to produce fluorescent clinopyroxenes for jewellery.

1. Introduction

The clinopyroxenes on the join $CaMgSi_2O_6$ (diopside)–$NaAlSi_2O_6$ (jadeite) are the most important minerals in petrology. The jadeitic clinopyroxenes and omphacites are composed largely or dominantly of these two components in solid solution (e.g. [1–3]). The clinopyroxenes of the diopside–jadeite join are interesting because of the relatively rare occurrence of the pure minerals formed in a high-pressure environment [4, 5]. Diopside–jadeite pyroxene is well known as a polycrystalline gemstone of great beauty and, potentially, of great toughness. Good-quality diopside–jadeite is more highly prized and rarely synthesized. Jadeite, which is well known as an end component on the join diopside–jadeite clinopyroxenes, has been synthesized for jewellery [6–8].

A variety of clinopyroxenes on the join $CaMgSi_2O_6$–$NaAlSi_2O_6$ has been synthesized in many laboratories [9, 10] in the past decades. However, the above synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ pyroxenes, which were used to investigate their physical and chemical properties, could not be used as jewellery, because the samples were not in pieces of gem quality and size, as far as we know.

In the solid solution of $CaMgSi_2O_6$(Di)–$NaAlSi_2O_6$(Jd) clinopyroxenes, near the 1 : 1 composition, the cation ordering belongs to $P2/n$ space group [11–13]. The tetrahedral sites are occupied by Si^{4+} with a negligible amount of Al^{3+}, Al^{3+} and Mg^{2+} occur at the M1 octahedra, Na^+ and Ca^{2+} at the M2 octahedra. Heating experiments on above natural diopside–jadeite have shown that the long-range ordering disappears rather abruptly between 700 and 750 °C, as suggested by Fleet *et al.* [14].

The diopside–jadeite is broken down to nepheline and plagioclase at 750 °C in accordance with the following equation

$$\underset{\text{diopside–jadeite}}{CaMgSi_2O_6\text{–}NaAlSi_2O_6} \rightarrow \underset{\text{nepheline}}{NaAlSiO_4} + \underset{\text{plagioclase}}{CaMgSi_3O_8} \qquad (1)$$

Structurally, the key change here is the six-fold to the four-fold coordination of Al^{3+}. Therefore, at 1 atm, diopside–jadeite is in the metastable form as well as jadeite. However, it retains its primative structure if not heated, because a major structural change is required for dissociation. Jadeite is well known as a high-pressure mineral which forms under a pressure of > 20 kbar in order to stabilize the Al^{3+} in six-fold coordination in the presence of Si^{4+} [15]. The solid solution of the $CaMgSi_2O_6$ component in jadeite lowers the pressure at which sodic pyroxene becomes stable [16].

The phase equilibrium data were given by Kushiro [17], by Bell and Kalb [18], and by Ganguly [19] on diopside–jadeite solutions coexisting with plagioclase and quartz at high temperatures and pressures. However, the stability regions of diopside–jadeite

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pyroxenes were reapproached in our experiments. In addition, it was the purpose of this investigation to synthesize materials of gem quality and size. The syntheses of diopside–jadeite clinopyroxenes for jewellery were carried out on the bases of phase diagrams of our investigation. All the above syntheses used modern high-pressure equipment, a cubic anvil press.

2. Experimental procedure

The different shades and colours of the resulting diopside–jadeite pyroxenes for jewellery were synthesized from glasses by a phase transformation under high temperatures and pressures. The synthetic compositions (molar per cent) are $Di_{1-x}Jd_x$ ($x = 1.0, 0.9, 0.8, 0.7$, and 0.6). Glasses of the desired various compositions were made by fusing reagents Na_2CO_3 (99.8%), SiO_2 (99.0%), Al_2O_3 (99.9%), MgO (99.9%), and $CaCO_3$ (99.0%) in the proper proportions in order to make the total composition $Di_{1-x}Jd_x$. The above mixtures were melted in a platinum crucible in air in the temperature range 1350–1550 °C. The molten liquid was cooled quickly in ice–water. The quenched glass was broken out and crushed, then refired as many times as required to produce a homogeneous product. Because the viscosity of the liquid was quite high even at 1350 °C [20], homogeneity is a problem, especially when other oxides are added to control the colour of the resulting samples.

A small amount (0.15–2.0 wt %) of Cr_2O_3 is a principal colouring agent to obtain the typical green colour of diopside–jadeite gemstones. The intensity of the colour – light or dark (almost black) – is controlled by the amount of Cr^{3+} in the resulting products. This, in turn, is dependent on the concentration of the original chromium as Cr_2O_3. In initial mixtures, more than 1.5 wt % Cr_2O_3 yields a dark colour of the resulting samples, while more than 2 wt % yields black. On the other hand, less than 0.3 wt % Cr_2O_3 yields a light green or white colour in the final products. In the proportions of 0.4–1.0 wt %, Cr_2O_3 yields a typical green or emerald colour in the resulting diopside–jadeite pyroxenes for jewellery.

Other oxides such as Co_2O_3 and NiO_2, Fe_2O_3, TiO_2, MnO, CuO, FeO–Cr_2O_3, etc., were also added in different proportions to obtain the various colours of the resulting products, as shown in Table I. In addition, small amounts (0.01–2.0 mol %) of rare-earth oxides were added to produce fluorescent stones. For example, CeO_2 was added to produce violet fluorescence; Nd_2O_3, blue; Sm_2O_3 and Dy_2O_3, yellow; Pr_6O_{11} and Lu_2O_3, green; Eu_2O_3, red; Er_2O_3, pink. Combinations of CuO–Eu_2O_3 and Co_2O_3–Nd_2O_3, Cr_2O_3–Pr_6O_{11}, Cr_2O_3–Lu_2O_3, etc., were also added to produce some colour variations which combined fluorescence with visible light colours (see Table II).

All quenched glasses after homogenization were found to correspond to the expected stoichiometries within the analysis error limits, which averaged ± 0.3% absolute. The glass was crushed to a 60–120 mesh powder as shown in Fig. 1 and used in this form for conversion to diopside–jadeite clinopyroxene by a crystallization process in its stability region. The powdered material was placed in a high-pressure cell with a graphite sleeve as a container and heater as shown in Fig. 2. The cell and its contents were held under varying pressures of 10–55 kbar and in the temperature range 800–1900 °C in the stability region of diopside–jadeite pyroxene for periods of $\frac{1}{12}$–24 h. The temperature was then lowered to ambient conditions by shutting off the power to the cell; then the pressure was released. Quenched charges were examined by scanning electron microscopy and X-ray powder diffraction.

TABLE 1 Effect of various concentrations of different colouring agents in the initial mixtures on the colour of the final diopside–jadeite gemstone

Colouring agent	Amount (wt %)	Colour variation
Cr_2O_3	0.15–2.0	Light green to dark green
Co_2O_3	0.10–1.0	Light green to dark green
Fe_2O_3	0.10–4.0	Lavender to brown
NiO	0.10–4.0	Light green to dark green
Cr_2O_3 + FeO	0.15–2.0	Light green to dark green
TiO_2	1.0–10.0	White and translucent
MnO	0.3–0.4	Lavender to violet
CuO	1.0–4.0	Light red to vermillion

TABLE II Various fluorescent colours of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ pyroxenes gem with various rare-earth oxides (0.01–2.0 mol) in initial mixtures emitted by u.v. radiation

Rare-earth oxide	Fluorescent colour
CeO_2	Violet
Pr_2O_3	Green
Nd_2O_3	Blue
Sm_2O_3	Yellow
Eu_2O_3	Red
Dy_2O_3	Yellow
Er_2O_3	Pink
Lu_2O_3	Green
CuO–Er_2O_3	Red
Co_2O_3–Nd_2O_3	Blue
Cr_2O_3–Pr_6O_{11}	Green
Cr_2O_3–Lu_2O_3	Green

In the experiments, pressure was calibrated on the electrical transition for bismuth (2.55 and 7.7 GPa), tantalum (3.7 GPa), and barium (5.5 GPa) at room temperature (see Lloyd [21]). The temperature of the sample was estimated from the electric power through the graphite sleeve heater and calibrated by inserting a 6% Rh · Pt–30% Rh · Pt thermocouple in the cell. The pressure effects of e.m.f. were uncorrected. The values of pressures and temperatures obtained were estimated to be accurate to within ± 0.2 GPa and ± 25 °C, respectively.

Unit cell parameters of the synthetic charges were determined by powder X-ray diffraction and refined by least squares. CuK_α radiation and a diffractiometer scan rate of 1/2° 2θ per minute were used. Calibration depended on an internal standard of monocrystalline silicon. 32 diffraction maxima in the range 10°–70° 2θ were used to calculate unit cell parameters of synthetic clinopyroxenes. Refinement of the crystal structure of the synthetic diopside–jadeite pyroxenes was also investigated by scanning electron microscopy (SEM).

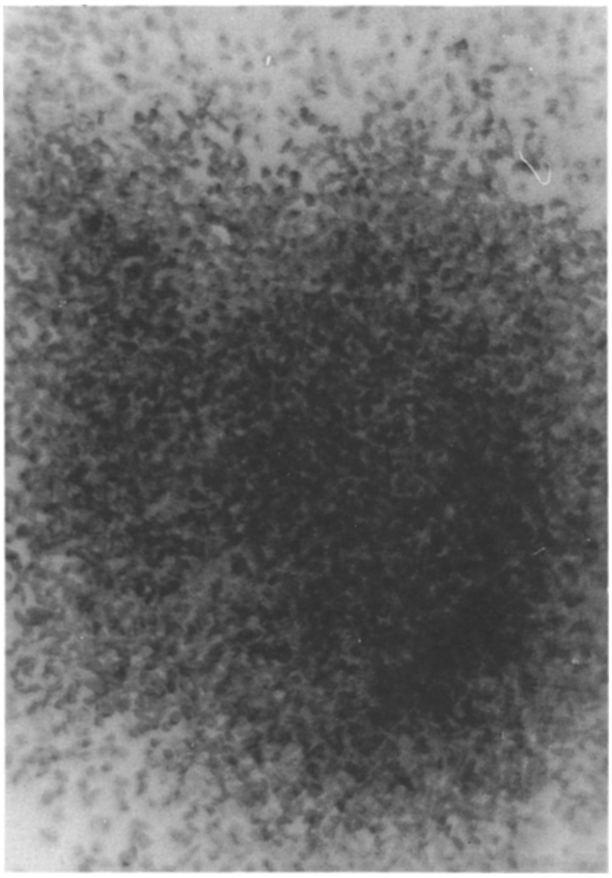

Figure 1 Photomicrograph showing enhedral synthetic diopside–jadeite crystals that have grown in a glass. The glass sample was removed from an experimental run that had been quenched to room temperature prior to complete crystallization of the glass.

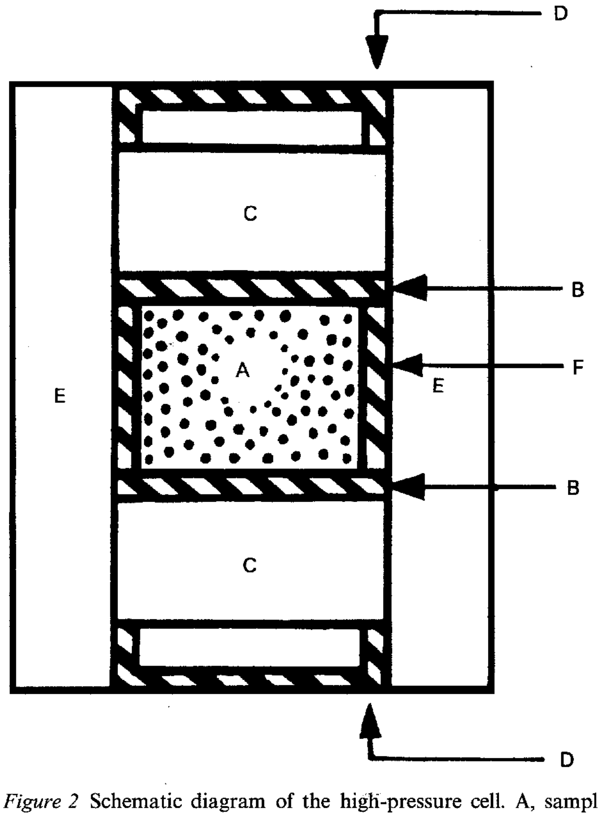

Figure 2 Schematic diagram of the high-pressure cell. A, sample area; B, graphite discs; C, bulk metal; D, electrode; E, insulation; F, graphite heater sleeve.

3. Experimental Results

3.1. The stability regions of diopside–jadeite clinopyroxenes

The samples were polished after synthesis. Identification and accurate characterization of the phases was made by powder X-ray diffraction. The analysed and observed results are plotted in Fig. 3. The experimental results reveal that the stability of 0.4 $CaMgSi_2O_6$–$0.6NaAlSi_2O_6$ clinopyroxene is higher than that of the pure sodic pyroxene $NaAlSi_2O_6$ under lower pressure. In other words, the minimum pressure converting glass of the composition $0.4CaMgSi_2O_6$–$0.6NaAlSi_2O_6$ to diopside–jadeite is lower than that to convert glass of the composition $NaAlSi_2O_6$ to jadeite. This result is more coincident with the estimate of Reinsch [16].

In our experiments, the phase equilibrium temperatures of jadeite and diopside–jadeite coexisting with nepheline + albite and nepheline + plagioclase, respectively, are higher than those of Bell and Kalb's experiments [18] under higher pressure: for example, a maximum of $\approx 100\,°C$ simultaneously for Jd and $Di_{0.4}Jd_{0.6}$ at 40 kbar, respectively. However, they are nearly consistent with each other under a relatively lower pressure, such as 30 kbar. They all are approximately 1360 and 1500 °C for Jd and $Di_{0.4}Jd_{0.6}$, respectively.

According to the observed results, the discs often have a black or a dark centre when the crystallizing conditions are below 1350 °C and 35 kbar, but the discs are hard, compact, and glossy, as shown in region C in Fig. 3. However, the discs are usually cracked and a white substance was produced on the surface after ageing. Only when both temperature and pressure were higher than 1350 °C and 35 kbar, respectively, could the synthetic discs be used for jewellery. The samples of gem quality were only obtained in region G. When the temperature and pressure are greater than 1450 °C and 45 kbar, respectively, the discs are bright and glossy, and had excellent colour after polishing. They were also hard and compact. The best discs were translucent. Several cylindrical pieces of various colours and shades have been polished in cabochon form as shown in Figs 4 and 5. Some of them have been mounted as pendants, earrings, tie pins, and rings, etc. Layered combinations of colours, such as green and white, were synthesized to simulate natural mottled and patterned diopside–jadeites. In this way, the synthetic discs are very similar to the natural one. The maximum size that we have attained so far is about 14 mm diameter and 8 mm thick. But this is a limit imposed only by the size of the cell that is available.

3.2. Unit cell parameters

The unit cell parameters of the discs in the gem-quality region were determined by X-ray powder diffraction and refined by least squares. Table III gives the unit cell parameters of the synthetic and natural $CaMgSi_2O_6$–$NaAlSi_2O_6$ clinopyroxenes. The unit cell parameters of the synthetic clinopyroxenes on the join

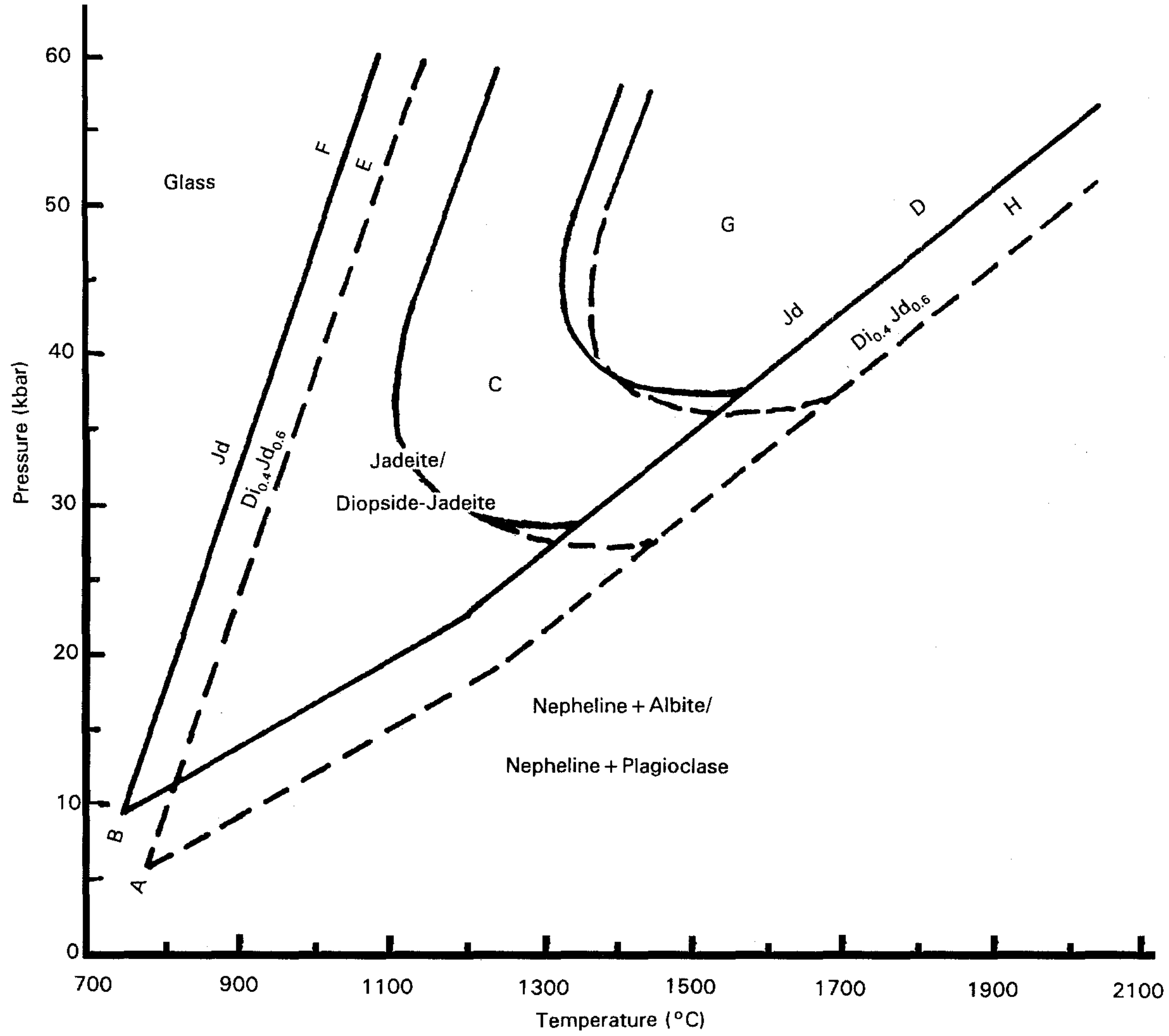

Figure 3 Phase diagrams of solid solution $NaAlSi_2O_6$ and $0.4CaMgSi_2O_6$–$0.6NaAlSi_2O_6$. Lines AE and BF indicate the growth of crystals $Di_{0.4}Jd_{0.6}$ and Jd from their composition glasses, respectively. Curves AH and BD are the phase equilibria of $Di_{0.4}Jd_{0.6}$ and Jd coexisting with nepheline + plagioclase and nepheline + albite, respectively. C = cracked and a white substance produced on the surface of the discs synthesized in this region after storing a long time, G = gem quality region.

Di-Jd are plotted against composition in Fig. 6. The unit cell volumes are nearly linear between the end members. The significant expansion of the *a*- and *b*-axes occurs with increase of the mole fraction of the diopside component in the jadeite, as well as the increase of the unit cell volumes, but there is little increase of the *c*-axis.

3.3. Physical properties

The physical properties of the solid solution of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ clinopyroxenes for jewellery such as hardness, toughness, density, and refractive index were measured (Table IV). Most of the discs were hard and tough. Their hardness was between 980 and 1018 kgf mm^{-2} (Mohs Scale hardness H6.7–6.8). The maximum hardness was about 1088 kgf mm^{-2} (H6.94). In general, the hardness of natural $CaMgSi_2O_6$–$NaAlSi_2O_6$ system pyroxenes is about H6.5–7.0. The fracture toughness of most discs was approximately 7.24×10^8 dyn $cm^{-3/2}$. This result is more consistent with the investigation of Bradt *et al.* [23].

The density and index of refraction of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ clinopyroxenes for jewellery were measured by a conventional Archimedes method using water at 20 °C in air. The density of most discs was between 3.26 and 3.34 g cm^{-3}. The refractive index was between 1.66 and 1.67. In general, the density and refractive index of natural $CaMgSi_2O_6$–$NaAlSi_2O_6$ solid solution clinopyroxenes are 3.22–3.43 g cm^{-3} and 1.66, respectively.

3.4. Microstructure of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ pyroxenes

The fracture surfaces of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ solid solution clinopyroxenes were observed by SEM and are shown in Fig. 7. The observed results reveal that they all have a similar texture which is an intergranular fibrous crystal. This type of the fibrous texture is the same as that described by Carpenter [22] and by Bradt *et al.* [23].

4. Discussion

DeVries and Fleisecher [6] reported that delamination took place at right angles to the axis of the press when the pressure was released from a uniaxial press.

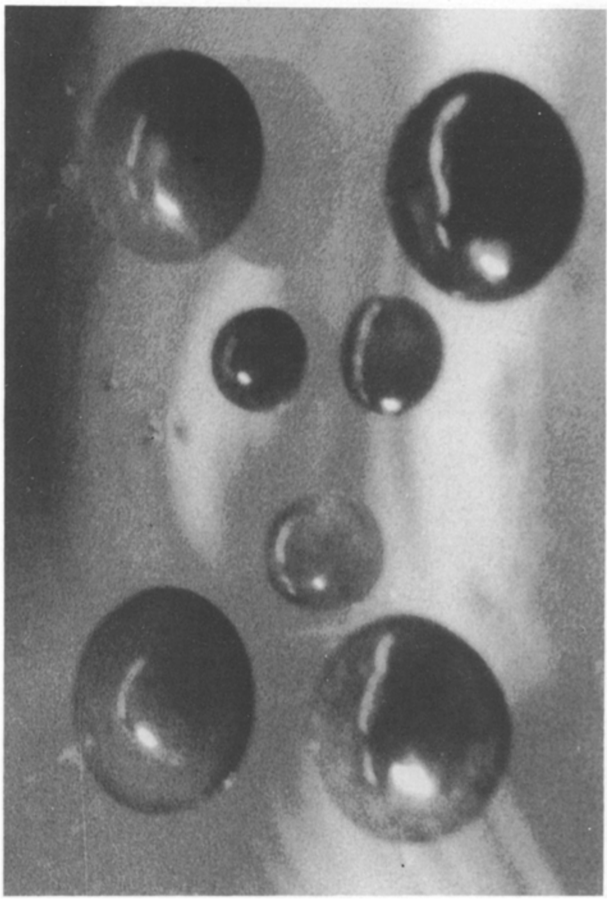

Figure 4 Synthetic diopside–jadeite discs resulting from the regions C shown in Fig. 3. The sample numbers of the diopside–jadeites, starting at the top and from left to right, are as follows: 1, 2, 3, 4, 5, 6, 7. The maximum weight (no. 7) is 7.62 ct. The best discs (nos 3, 4, and 5) were translucent.

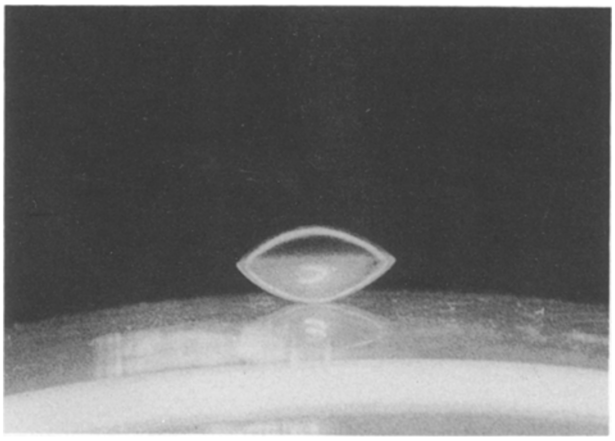

Figure 5 Cabochon of synthetic emerald diopside–jadeite (no. 2). Cabochon dimensions: diameter 12 mm; thickness at centre 6 mm.

However, the delamination of the discs hardly appeared in our experiments, even though the pressure was released quickly. The reason for the above result may be that the cubic anvil press has an advantage over the Girdle or Belt press in making better sintered $CaMgSi_2O_6$–$NaAlSi_2O_6$ solid solution clinopyroxenes for jewellery because it released its pressure simultaneously from the triaxial press at the same rate.

A radial temperature gradient is also created by indirect heating (as with a graphite sleeve), which can lead to problems in homogeneity across the sample – sometimes a translucent diopside–jadeite pyroxene with an opaque centre. To help lessen the opaque centre it was found useful to add two bulk metals on the ends of the samples. But the real reason for the above phenomenon was not clear.

The textures of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ solid solution clinopyroxenes were in contrast with that of the natural one (as shown in Fig. 7). The interpenetrating fibrous grains of the synthetic sample were much thinner than those of the natural one, and their arrangement was not as highly ordered as that of the natural one. The boundaries among the interpenetrating fibrous grains of synthetic $CaMgSi_2O_6$–$NaAlSi_2O_6$ clinopyroxene were more clear. Attempts were made to reduce the number of grain boundaries and to expand the interpenetrating fibrous grains. We observed that grain boundaries became blurred and the grains were also smoothly continued under the elevated pressures. Thus, the number of grains boundaries in the unit volume of diopside–jadeite crystal become less.

The length of duration of the glass material remaining at the region of nucleation was controlled to obtain different numbers of nuclei. The shorter the duration of the glass material at the nucleation region, the fewer nuclei were formed in the unit volume. Thus, the crystalline temperature was elevated to the temperature of the crystal growth region as quickly as possible. The nuclei were developed into crystals. The number of the interpenetrating fibrous grains in the unit volume of the crystal was consequently less. In other words, the interpenetrating fibrous grains were

TABLE III Unit cell parameters of synthetic clinopyroxenes on the join $CaMgSi_2O_6$(Di)–$NaAlSi_2O_6$(Jd) and natural jadeite

	a (nm)	b (nm)	c (nm)	β (deg)	V (10^{-3} nm^3)
$Di_{0.4}Jd_{0.6}$	0.9539	0.8758	0.5233	107.08	417.40
$Di_{0.3}Jd_{0.7}$	0.9514	0.8708	0.5231	107.13	414.21
$Di_{0.2}Jd_{0.8}$	0.9487	0.8657	0.5230	107.19	411.02
$Di_{0.1}Jd_{0.9}$	0.9463	0.8617	0.5227	107.23	407.54
$Di_{0.0}Jd_{1.0}$	0.9439	0.8578	0.5225	107.28	404.02
Natural Jd[3]	0.9428	0.8568	0.5226	107.59	402.40
Synthetic Di[24]	0.9745	0.8925	0.5249	105.87	439.08

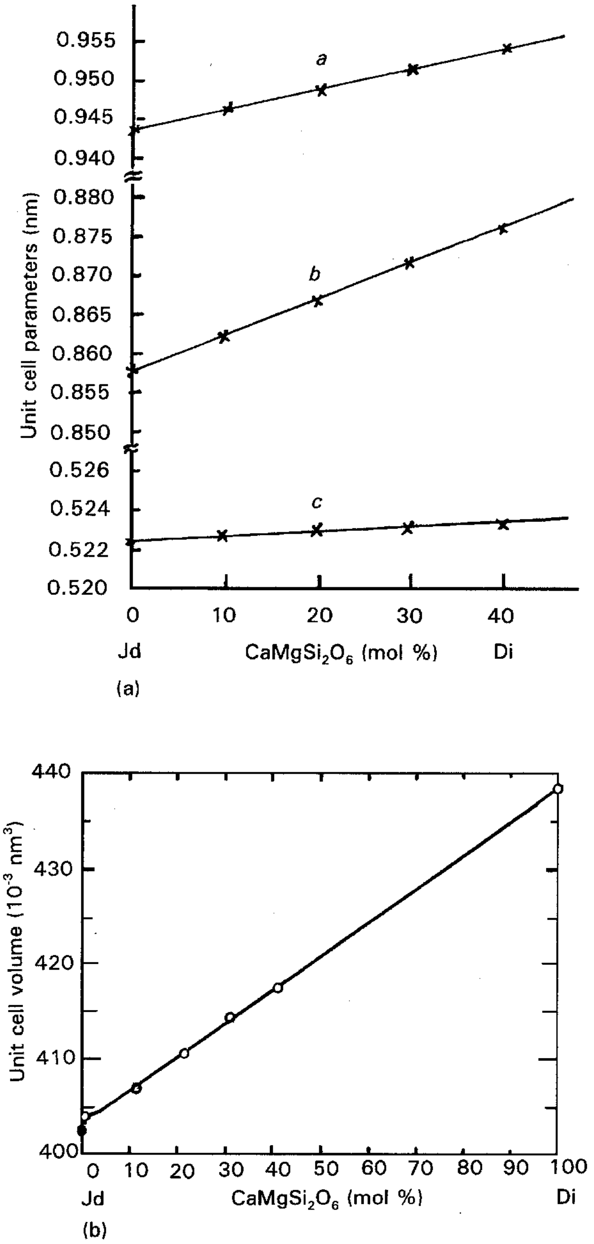

Figure 6 (a, b) Unit cell parameters of synthetic Jd, $Di_{0.1}Jd_{0.9}$, $Di_{0.2}Jd_{0.8}$, $Di_{0.3}Jd_{0.7}$, $Di_{0.4}Jd_{0.8}$, and natural Jd. (○) Synthetic clinopyroxenes crystallized from glass at 45 kbar and 1450 °C. (●) Natural jadeite.

thicker. At the same time, the thicker fibrous grains reduce the number of grain boundaries in the unit volume of the crystal. As a consequence, the times for light to pass through the grain boundaries were reduced, and the transparency of the diopside–jadeite discs was somewhat improved.

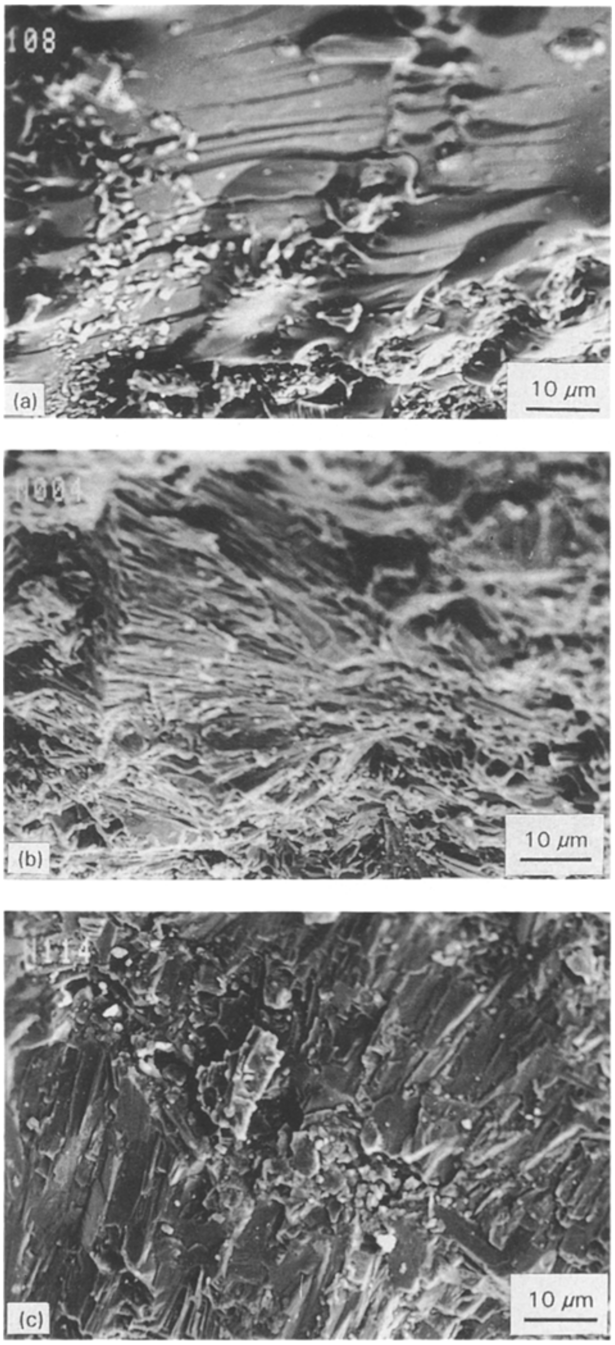

Figure 7 Scanning electron micrographs of the fracture surfaces of glass, synthetic $Di_{0.4}Jd_{0.6}$, $Di_{0.2}Jd_{0.8}$, Jd and natural Jd. (a) Non-crystalline material resulting from an experimental run that had been quenched from 50 kbar and 1000 °C to ambient conditions prior to crystallization of the glass; (b–d) synthetic $Di_{0.4}Jd_{0.6}$, $Di_{0.2}Jd_{0.8}$ and Jd, respectively; (e) natural Jd.

TABLE IV Physical properties of synthetic $CaMgSi_2O_6$(Di)–$NaAlSi_2O_6$(Jd) clinopyroxenes

	Density ($g\,cm^{-3}$)	Hardness (Mohs Scale H)	Fracture toughness (10^8 dyn $cm^{-3/2}$)	Refractive index
Synthetic DiJd	3.26–3.34	6.70–6.94	7.24	1.66–1.67
Natural Jd	3.22–3.43	6.50–7.0	7.10	1.66
Natural Di	3.22–3.38			

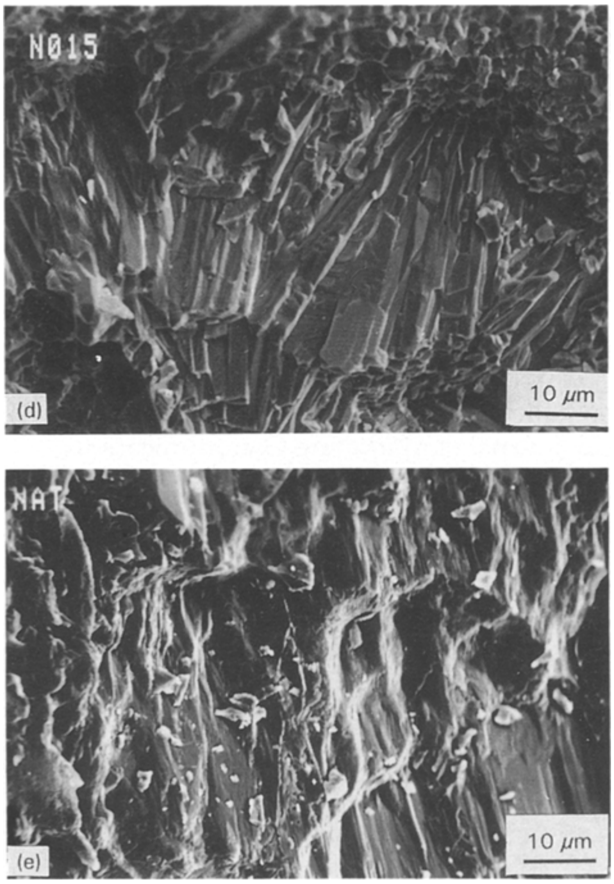

Figure 7 (continued).

5. Conclusions

1. The syntheses of clinopyroxenes on the join of the diopside–jadeite system were carried out in high-pressure equipment – a cubic anvil press – in the temperature range 800–1900 °C and under varying pressures of 10–55 kbar. From these experiments, the stability regions of various compositions of diopside–jadeite have been established, and gem-quality regions identified.

2. Using the available *P–T–X* data as guidance, attractive pieces of diopside–jadeite have been made. The microstructure and physical properties of the synthetic gem diopside–jadeite are the same as natural diopside–jadeite.

3. The different colours and shades of diopside–jadeite for jewellery have been achieved by adding different kinds of colouring agents. In addition, the rare-earth oxides were also added to produce fluorescent stones.

4. The crystallizing conditions of diopside–jadeite for jewellery were greater than 1350 °C and 35 kbar. Some of the discs were bright, glossy, hard, compact, and translucent. The maximum size of synthetic diopside–jadeite produced here for jewellery was 14 mm diameter and 8 mm thick.

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