American Mineralogist, Volume 65, pages 381–389, 1980

Czochralski growth of single-crystal fayalite under controlled oxygen fugacity conditions[1]

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Abstract

Single-crystal boules of fayalite (Fe_2SiO_4) were grown in the temperature range 1165 to 1200°C at 1 bar total pressure from high-purity oxide melts of 1.95:1 to 2.10:1 Fe:Si atom ratio. A modified Czochralski technique was used, with platinum crucibles inductively heated under oxygen fugacities, $f(O_2)$, between 10^{-9} and 10^{-12} bar. The boules are up to 10 mm in diameter by 40 mm long and brownish-black in color. The best crystal homogeneity was obtained at growth rates of ≤ 3 mm/hr from 2.1:1 Fe:Si melts at an $f(O_2)$ of 10^{-12} bar at 1180 to 1185°C. Colorimetric data indicate boule Fe^{3+} contents which increase with synthesis $f(O_2)$ from 0.27% (10^{-12} bar) to 0.86% (10^{-9} bar). The typical orthorhombic unit-cell parameters are $a \doteq 4.8214$ to 4.8219, $b = 10.4774$ to 10.4767, and $c = 6.0880$ to 6.0893Å, varying slightly with synthesis $f(O_2)$. The optical and infrared absorption spectrum is similar to that of natural fayalite, exhibiting a broad absorption band at 10,000Å with transparency maxima at 7,000 and 25,000Å. Samples appear stable up to melting at ~1202°C[$f(O_2) \approx 10^{-12}$ bar], but lose weight and solidify incongruently.

Introduction

The growth of good-quality single crystals containing iron, whose valence state is controlled by the oxygen fugacity prevalent during growth, is not easy to achieve. Many important physical properties of such phases may vary dramatically with Fe^{3+}/Fe^{2+} ratio. One such phase, of importance in both mantle studies and metallurgy, is fayalite (ideally, Fe_2SiO_4). Unfortunately, large fayalite single crystals have not been as available as are those of forsterite (Finch and Clark, 1971) or those of other olivine-structure phases (*e.g.*, Finch *et al.*, 1975; Takei, 1976). The paucity of single-crystal studies on fayalite has been due chiefly to the lack of well-characterized, homogeneous samples. Recently, Takei (1978) described the melt growth of fayalite single crystals by a lamp-image, floating-zone technique, and referenced previous fayalite crystal-growth work.

Based on our experience with the manganese olivine, tephroite (Mn_2SiO_4), we developed a Czochralski technique for producing fayalite boules up to 10 mm in diameter by 40 mm in length (Finch and Kopp, 1977, p. 28). In contrast to tephroite, the melt growth of fayalite was believed to be complicated by incongruent melting behavior (Bowen and Schairer, 1932) and by uncertainties regarding its Fe^{3+} content. This article describes our growth method, and compares the crystal properties with those of fayalite listed in the literature. Some of our crystals are being used in studies of physical properties, including electrical conductivity, infrared absorption, high-temperature creep, compressive strength, shock-wave propagation, *etc.*

In the Czochralski method, a single-crystal seed is inserted into a melt of the proper composition and temperature. The seed is then slowly withdrawn while it is rotated about the growth axis. Under carefully controlled conditions the crystal which is produced (called a boule) will be a single crystal. The Czochralski method has not been generally em-

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[1] Research sponsored by the Division of Basic Energy Sciences, United States Department of Energy, under contract W-7405-eng-26 with the Union Carbide Corporation.

0003–004X/80/0304–0381$02.00

ployed for the melt growth of materials with poor radiant-heat transmission and low thermal conductivity such as fayalite, since heat transfer through the growing boule is low, and a thermal geometry promoting efficient growth is difficult to achieve. However, Horn (1961) used the method to grow ferrites, Burmeister (1966) to grow wüstite, and Ginley and Baughman (1976) to grow several iron titanates. The Czochralski technique allows direct observation of growth under widely differing conditions (melt composition, thermal geometry, ambient gas, *etc.*), and affords growth on a freely rotating seed without the crucible removal difficulties frequent in Bridgman–Stockbarger methods (Laudise, 1970, p. 164).

Synthesis

The fayalite boules were grown in the temperature range 1165 to 1200°C at 1 bar total pressure from oxide melts of 1.95:1 to 2.10:1 Fe:Si atom ratio. A modified Czochralski system was used, with inductively heated (450-kHz) platinum crucibles. In most runs, a current of Ar–4% H_2 (by volume), bubbled through 3 cm of H_2O at ~25°C at 5–10 cm^3/sec, flowed through the initially evacuated growth chamber, which according to Deines *et al.* (1974, p. 77) provides an effective oxygen fugacity of 10^{-12} bar during growth. This atmosphere ensures the stability of Fe^{2+}, with minor amounts of Fe^{3+} (Muan, 1955). The system (Fig. 1) includes an adjustable, ZrO_2-insulated, iridium radiant heat shield, supported by an inlet gas cooling tube. The shield is necessary because fayalite has low thermal conductivity and transmits radiant heat poorly at 1200°C (Fukao *et al.*, 1968). Shielding the boule from thermal radiation and preventing heat loss from the open melt promote growth on the boule without spurious nucleation and freezing of the surrounding melt. Gas cooling of the boule encourages faster heat transfer (higher dT/dx in growth direction). The optimal growth parameters are given in Table 1.

The starting material was pelletized from mixtures of high-purity (99.999 + %) Fe_2O_3 and SiO_2 powders (Johnson–Matthey Chemicals, Ltd.). For loading convenience, the pellets were densified by fusing in a reducing gas flame. At least 10 hours of initial melt equilibration in the apparatus at ~1250°C are re-

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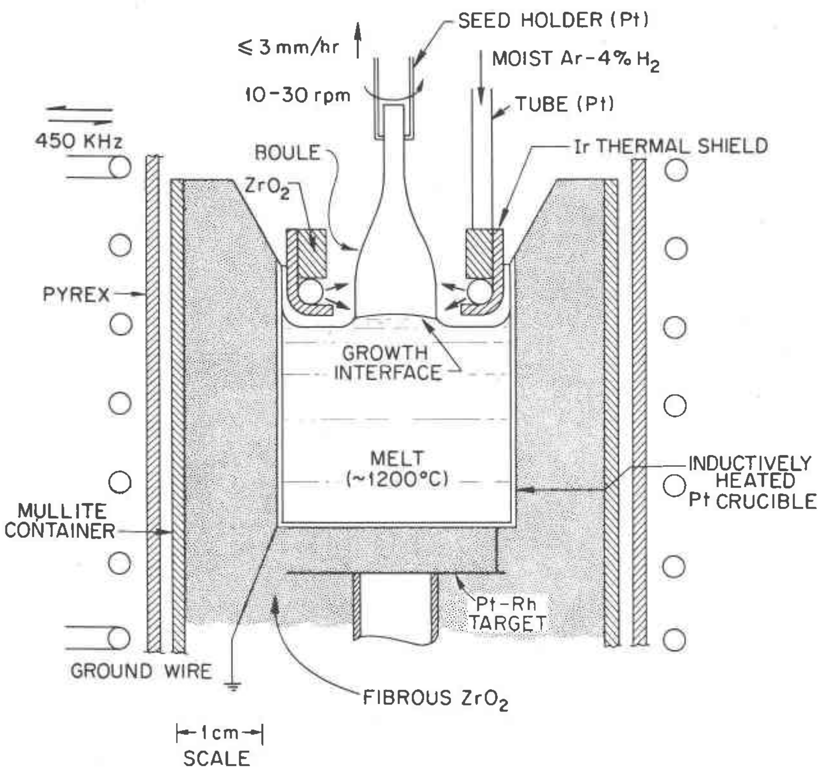

Fig. 1. Czochralski system for the growth of fayalite.

Table 1. Optimal Czochralski growth conditions for fayalite

Parameter	Growth Conditions
Melt Fe:Si	2.05:1 to 2.1:1
Atmosphere (flow rate)	Ar–4 percent (volume) H_2–1.5 percent (volume) H_2O (5–10 cm^3/s)
Oxygen fugacity (at 1200°C)	10^{-12} bar*
Crucible	20-ml, Fe-saturated platinum
Thermal shield	annular, iridium; ZrO_2– insulated
Melt temperature:†	
growth interface	1180–1185°C
crucible wall	1210–1250°C
Boule rotation	10–30 rpm
Boule lift rate	≤3 mm/h
Seed orientation	[100]

*Deines et al. (1974).

†Uncorrected optical pyrometer.

quired in a moist Ar–4% H_2 atmosphere to reduce most of the original Fe_2O_3 to FeO. More rapid equilibration is possible in moist Ar–10% H_2, and is marked by the appearance of bright flecks (metallic Fe) and glassy segregate (SiO_2) on the melt surface within 5 hr. With subsequent change to moist Ar–4% H_2 for crystal growth, the melt becomes homogeneous. The approach to equilibrium may be judged both by the appearance of the melt and the ease of establishing growth when a seed is inserted into the melt. Attempts to prepare large quantities of melt using elemental Fe resulted in premature crucible failure.

It is known that fayalite crystallizes from Fe^{3+}-containing melts (Bowen and Schairer, 1932). This was supported by our observation of numerous magnetite (Fe_3O_4) crystallites in solidified melts from which good-quality fayalite crystals had been grown. The platinum crucibles were readily wet by the melt and gradually absorbed Fe under moist Ar–4% H_2. However, the maximum crucible temperature (~1250°C) was considerably below the solidus (~1500°C) of the Fe–Pt system (Hansen, 1958, p. 698). Although the exposed crucible surfaces soon became iron-saturated, the crucible lifetime was usually >150 hours under the $f(O_2)$ conditions used. A typical 80 g, 0.5 mm-wall crucible (~35 cm^2 exposed to 100 g of melt) showed a weight gain of ~4 g, attributed to Fe absorption, after 150 hours of exposure. Incremental additions of Fe_2O_3 to the melt had a beneficial effect on growth, compensating for the loss of Fe to the crucible and maintaining a melt Fe:Si ratio favorable to good growth. The rate of supplemental Fe_2O_3 additions depended on melt history, growth behavior, and the $f(O_2)$ used. The cumulative amount added seldom exceeded 5% (by weight) of the original charge.

Temperature control was on the basis of the signal from an optical pyrometric thermopile, sighted at a Pt–20% Rh target below the crucible (Fig. 1). A constant gas flow rate was necessary for the best growth results, since this rate affects both the rate of heat transfer through the boule and the rate of fayalite deposition from the melt. The optimum flow rate was determined empirically. Higher flow rates increased the growth rate, but at the expense of crystal perfection. As the melt level decreased, the iridium shield was gradually lowered to maintain an interval one to two millimeters above the melt surface, care being taken to avoid direct contact with the melt. Surface temperatures were measured with an optical pyrometer (uncorrected), and were reasonably consistent (±5°C) with thermocouple measurements at the melt surface. Good quality growth was obtained with melt temperatures of 1180–1185°C at the boule periphery and 1210–1250°C at the crucible wall. The boule temperature was ~1140°C 0.5 cm above the melt surface, suggesting an interface dT/dx of 80–90°C/cm in the growth direction. The oxygen fugacity was monitored with a calibrated ZrO_2 electrolyte cell and the fugacities determined were consistent with those computed on the basis of hygrometer readings of ~1.5 vol % H_2O.

Although growth rates as high as 6 mm hr were attempted, they were difficult to maintain and normally resulted in poor growth (many voids and inclusions). The growth rate typically used was 3 mm/hr and produced good-quality, homogeneous material. Several runs at 1 mm/hr gave only a modest improvement in perfection over the 3 mm/hr rate. The use of additional thermal shielding (or afterheaters) above the melt resulted in a slightly less concave (to the solid) growth interface, but at the expense of slower growth rates (≤1 mm/hr) and poorer visibility of the growth interface.

The position of the induction coil relative to the crucible affected the system thermal geometry, and the optimal placement was determined empirically. A high coil/crucible position produced a quiet melt having little thermal convection (easier for seeding). The converse was true with a low coil/crucible placement (advantageous for melt equilibration). Boule rotation ranged between 15 and 30 rpm, faster rotation giving better stirring and a smoother, slightly less concave (to the boule) interface.

Abrupt changes in growth rate, $f(O_2)$, or temperature usually led to the formation of voids and/or magnetite inclusions in the crystals. Maintaining uniform conditions was essential to the growth of fayalite crystals with optimum homogeneity and perfection.

The growth directions used were [100], [010], and [001]. The seeds were cut from X-ray oriented single-crystal boules obtained by conventional Czochralski "neck-down" procedures (Laudise, 1970, p. 174). Rapid seed dissolution occurred when the seeding of insufficiently equilibrated melts was attempted. Seeds cut in a [100] direction gave boules with longitudinal (010) and (021) facets, allowing easy orientation. Boule dimensions ranged between 5 and 10 mm in diameter and up to 40 mm in length. Growth appeared easier to control in the [100] than in the [010] and [001] directions, and initiation of growth (attainment of adequate heat transfer through the seed) was easier with a >2-cm long seed having a diameter >75% of the shield aperture diameter.

Good-quality, single-crystal boules could be cooled to room temperature in the growth atmosphere in one-half hour with no apparent cracking. Isothermal annealing for >10 hr in a post-growth afterheater zone at ~1000°C, with subsequent cooling at ≤100°C/hr, was occasionally performed to reduce crystal strain. Several boules were grown under moist Ar–1% H_2 [$f(O_2) = 10^{-11}$ bar] and under the CO_2–H_2–N_2 atmosphere [$f(O_2) = 10^{-9}$ bar] used by Takei (1978). These experiments produced homogeneous material, although crystals appeared to contain slightly greater amounts of Fe^{3+} than those grown at an $f(O_2)$ of 10^{-12} bar.

Characterization

General

The physical properties of our crystals are compared with those of natural fayalite (Deer *et al.*, 1962, p. 2) and Takei's fayalite in Table 2. Our X-ray data were obtained both by diffractometer and Debye-Scherrer powder methods, using Cu*Kα* radiation (λ = 1.54178Å) and MgO as an internal standard. The data were refined using a least-squares extrapolation program. The optical absorption spectrum, obtained with a Cary 14H spectrophotometer between 4,000 and 25,000 (Fig. 2), differs slightly from the spectra reported for natural fayalite (Burns, 1970), but exhibits similar regions of increased transparency at 7,000 and 25,000Å, with a single broad absorption band centered near 10,000Å.

The black color and "opaque" nature of our boules suggested that they contained Fe^{3+} (Wickersheim and Lefever, 1962). We were surprised when Mössbauer (Fig. 3) and electron paramagnetic resonance studies indicated Fe^{3+} levels below their limits of detection (2% and 10 ppm, respectively). A preliminary colorimetric analysis also indicated an Fe^{3+} level <0.1%, but later colorimetric analyses with a more sensitive technique (thiocyanate complexing) revealed maximum Fe^{3+} contents between 0.27% and 0.86% (Table 3). Other impurities in our crystals were determined by emission and neutron activation spectroscopy (Table 3).

Table 2. Properties of synthetic and natural fayalities

Property	This Work	Takei*	Natural†
Hardness (001)	6-1/2 (Mohs) 248 (DPH)		6-1/2
Predominant cleavage	{010}	{010}	{010} {100} weak
Lattice parameters (Å):‡			
$f(O_2) = 10^{-12}$ bar	a_0 4.8214(3)		
	b_0 10.4774(7)		
	c_0 6.0880(2)		
$f(O_2) = 10^{-9}$ bar	a_0 4.8219(4)	4.821(8)	
	b_0 10.4767(8)	10.481(4)	
	c_0 6.0893(3)	6.097(7)	
			a_0 4.817(5)
			b_0 10.477(5)
			c_0 6.105(5)

*Takei, (1978).

†Deer, Howie and Zussman (1964).

‡X-ray diffraction at 25°C, Debye-Scherrer method (λ = 1.54178 Å)

Growth imperfections

Examples of the growth imperfections in our fayalite are shown in Figures 4 (reflected light) and 5

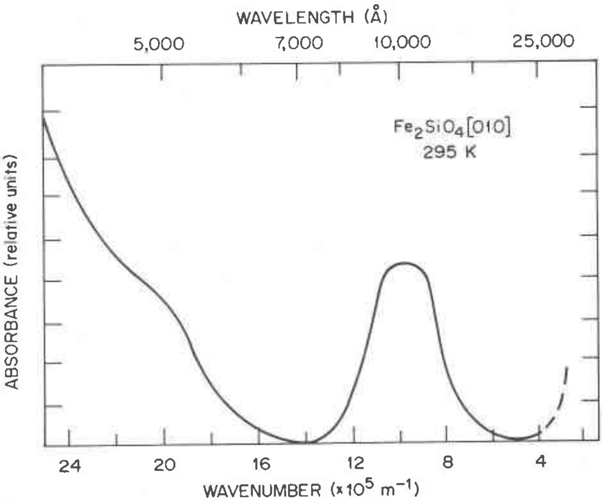

Fig. 2. Optical and infrared absorption spectrum of Czochralski-grown fayalite in the [010]. Boule 15254, sample thickness 0.2 mm.

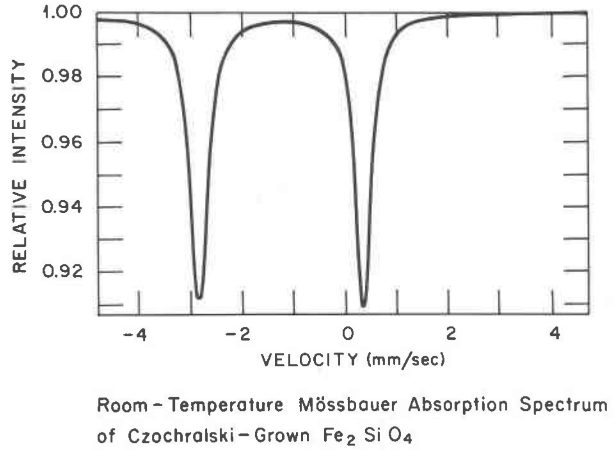

Fig. 3. Mössbauer absorption spectrum of Czochralski-grown fayalite. The two inverted peaks are due to Fe^{2+} at M1 and M2 octahedral sites. Noticeable asymmetry of the right peak would be produced by Fe^{3+} concentrations exceeding 2 percent.

(transmitted light). The growth conditions for the boules shown are given in Table 4.

In reflected light, the most common imperfections are regions of cellular growth (Figs. 4a, Boule 15226, longitudinal section and 4b, Boule 15224, transverse section through tip) and voids (Fig. 4b and 4f). The former occur as a result of minor imbalances in the bulk melt composition. An irregular or cellular interface develops between the growing fayalite crystal and the melt. Portions of melt (which incorporate rejected excess Fe^{3+}) with a composition nearer the eutectic composition become trapped in the cusps of the developing cells, and crystallize both fayalite and magnetite when the temperature drops below the eutectic temperature. The individual cells remain in crystallographic continuity (*i.e.*, they do not represent sub-grains within the boule). Voids are thought to be associated with the evolution of oxygen gas from the melt. Although some voids are observed in almost every boule, they occur most abundantly at the boule tip (Fig. 4b) and along the outermost surface of the boule (Fig. 4f). The development of both cells and voids is influenced by the bulk composition of the melt, the growth temperature, and the ambient gas composition. Both imperfections can be minimized by careful control of the experimental parameters and by the avoidance of too rapid changes in conditions.

Larger magnetite inclusions also occur. Although they may appear as isolated crystals, bands of magnetite crystals are occasionally arrayed transverse to the growth direction (Fig. 4c, Boule 15217, longitudinal section). The origin of these bands may be associated with an increase of Fe^{3+} in the melt due to $f(O_2)$ changes in the system imposed when the operator changes the growth conditions (temperature, lift, rotation, shield position, *etc.*).

Magnetite dendrites (Fig. 4d, Boule 15246) occur less frequently. They also represent a form of eutectic growth, but differ from the cellular growth shown in Figure 4a. The oriented nature of the dendrites suggests that they had nucleated in the fayalite but were growing in front of the matrix. This feature attests that the local melt composition had shifted to the Fe-rich side of the eutectic composition.

A relatively rare form of imperfection consists of magnetite crystals and crystal clusters surrounded by regions which contain symplectic intergrowths (L. A. Taylor, personal communication, 1979) of fayalite, magnetite, and silica (Fig. 4e, Boule 15240), which are enveloped by fayalite. These complex intergrowths are generally restricted to the tip of the boule and are thought to represent the rapid breakdown of fayalite to quartz and magnetite as the temperature and $f(O_2)$ conditions cross the QFM buffer curve

Table 3. Impurity data for Czochralski-grown fayalite single crystals

	Emission Spectroscopy* (ppm)	Neutron Activation† (ppm)
Al	10	
Ca	20	
Co		7.6
Mg	5	
Mn	10	4.4
Mo	20	
Cr		6.5
Ti	5	
Ir		1.1
Pt	(<25)‡	
Zr	(<25)‡	
	Colorimetric (wt percent)§	
Fe^{3+}	0.27 to 0.51	$f(O_2) = 10^{-12}$ bar
	0.75 to 0.86	$f(O_2) = 10^{-9}$ bar

*Error limits: −50% to +100 percent.

†Error limits: ±5 percent.

‡These elements were not detected (detection limits).

§By thiocyanate complexing after sample dissolution in HCl sparged under argon. The values cited are upper limits, since some Fe^{3+} may have resulted from oxidation of Fe^{2+} during dissolution.

Table 4. Growth parameters of fayalite boules*

Boule No.	Estimated Melt Fe:Si Ratio	Minimum $f(O_2)$ (bar)†	Melt Temperature (°C)‡	Comments
15198	2.00:1.00	10^{-14}	1170–1175	Moist Ar–10 percent H_2;Fe in melt
15217	2.00:1.00	10^{-12}	1165–1170	Random orientation
15224	2:10:1.00	10^{-4}	1150–1155	Argon atm.
15226	2.10:1.00	10^{-12}	1185–1190	Melt not totally equilibrated; multi-grained
15232	2.10:1.00	10^{-12}	1170–1185	[001] growth-direction
15240	2.10:1.00	10^{-12}	1180–1200	[010] growth-direction
15246	2.10:1.00	10^{-9}	1170–1180	CO_2-N_2-H_2 atm.
15249	2.10:1.00	10^{-9}	1180–1185	CO_2-N_2-H_2 atm.
15254	2.10:1.00	10^{-12}	1180–1185	Best boule
15257	1.95:1.00	10^{-12}	1170–1185	SiO_2-rich melt

*Rotation was 15–30 rpm and lift rate 3 mm/h in all runs. Unless otherwise stated, all runs were in the [100] growth direction.

†Deines _et al_ (1974).

‡Optical pyrometer, relative values only.

during the cooling process. Similar incipient breakdown has been noted in portions of the solidified melt.

Under the range of growth conditions used, the rarest imperfection consists of metallic inclusions (composed primarily of iron with 1 to 1.5% silicon) which occur just below the outermost surface layer of one boule (Fig. 4f, Boule 15198, transverse section). These inclusions resulted from the introduction of excess hydrogen into the system [$f(O_2) \approx 10^{-14}$ bar], resulting in the reduction of Fe^{2+} to elemental iron and the diffusion of some silicon from the melt into the iron.

Some of the common growth imperfections observed in thin sections are illustrated in Figure 5. Banding (Fig. 5a, Boule 15232 and 5b, Boule 15249) is thought to reflect changes in the Fe^{3+}:Fe^{2+} ratio, and is often introduced when the operator attempts to change the diameter of the growing boule (lower the melt temperature) or otherwise alter the growth parameters. The concave (to the solid) interface is obvious. Figure 5a also shows a relatively dark, biconvex region at the boule tip which consists of solidified melt. Note the significant rejection of excess Fe^{3+} by the growing boule.

The effect of excess SiO_2 (2.5%) is shown in Figure 5c (Boule 15257). Although fayalite continues to grow, small amounts of silica glass appear as a second phase in a eutectic-like intergrowth with fayalite. (Note that the concave interface and solidified melt appear much the same as for Fe-rich melts.) This interference by silica, in conjunction with the absorption of iron by the crucible, makes it preferable to grow fayalite from slightly Fe-rich melts.

Figure 5d (Boule 15254) illustrates one of the best crystals grown during the period of study of growth conditions. The low quality of the starting seed appears to have had little effect on the quality of subsequent growth. Minor growth bands generally correspond to initial periods of decrease in melt temperature. The almost straight section close to the tip is nearly free from banding. An attempt to increase the boule diameter further resulted in the incorporation of excess Fe^{3+}. Note the solidified melt at the tip.

Some lineage is apt to occur as a result of growth at a concave crystal–melt interface. Lineage boundaries are visible as minute ridges on the exterior surfaces of the as-grown boules. Lineage could be minimized by careful seed selection, uniform temperature, and lift control, and by allowing only gradual increases in boule diameter. Defects associ-

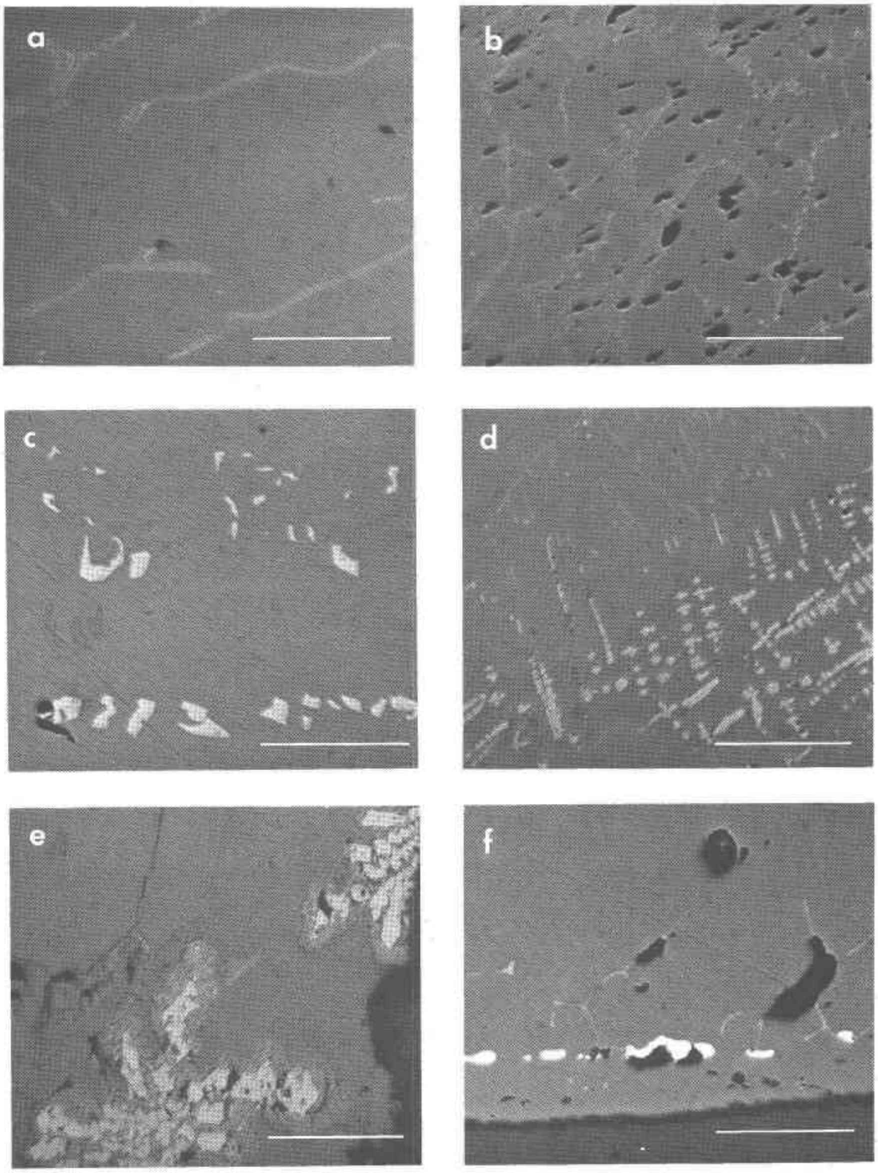

Fig. 4. Examples of growth imperfections observed with reflected light: cellular growth (a, b); prominent voids (b, f); magnetite inclusions (a, b, c, d, e); Fe–Si inclusions (f). Bar scale is 1 mm long.

ated with changes in boule diameter could be minimized by starting with a seed diameter approximating the desired boule diameter.

Discussion and conclusions

Comparison with method of Takei (1978)

Takei (1978) reported the growth of fayalite crystals which appear to be the first of adequate size for measurement of such properties as thermal conductivity, shock-wave propagation, *etc*. The Czochralski technique described here differs from Takei's in that it affords a substantially larger melt volume for accommodating rejected Fe^{3+} or stoichiometric imbalances. As a result, changes in melt composition are more gradual and probably less disruptive to homogeneous crystallization. The crystals prepared by Takei reportedly contained up to 0.6% Fe^{3+}, and were grown at an oxygen fugacity of 10^{-9} bar, several orders above the 10^{-12} bar used in most of our work. Our experiment under Takei's conditions produced fayalite with a maximum Fe^{3+} content of 0.86%.

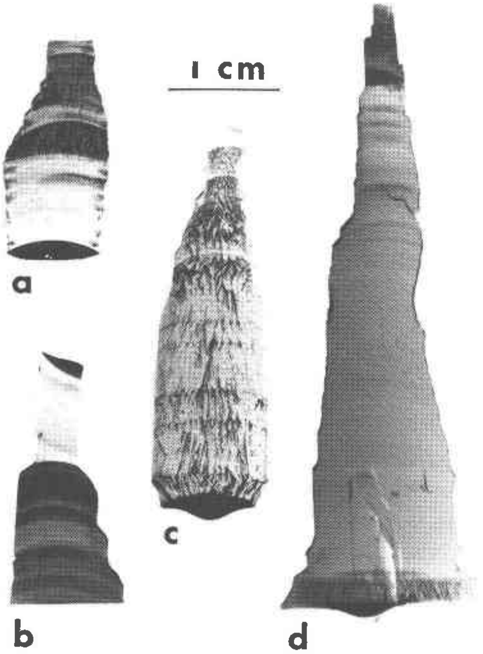

Fig. 5. Examples of growth imperfections observed in transmitted light: banding (a, b, d); interference by silica-rich phase (c); near optimal quality (d).

Takei reported his crystals to melt congruently. To evaluate the melting behavior of our crystals, we heated a 0.2 g portion of a boule [Fe:Si $\simeq$ 2.0:1; $f(O_2) \approx 10^{-12}$ bar] in a Mettler differential thermal/thermogravimetric analyzer system, using the moist Ar–4% H_2 growth atmosphere, platinum crucibles, and Al_2O_3 power as standard. No thermal effects or weight change occurred during initial heating (2°C/min) to sample melting at 1202°C. After melting, a slight weight loss began, perhaps as a result of loss of iron to the platinum crucible, and when the melt was cooled (2°C/min) the primary exothermic arrest occurred at 1190°C, followed by a smaller exothermic arrest at 1164°C, after which the weight loss ceased. The DTA/TGA curves are shown in Figure 6. While our DTA/TGA results are preliminary, they indicate that the sample melted congruently at 1202°C. After melting the sample began to lose weight (probably due to iron absorption by the cup and the concomitant oxygen loss). During subsequent solidification, the liquidus was intercepted at 1190°C (the melt now being slightly depleted in Fe but also slightly enriched in Fe^{3+}) and crystallization was complete at 1164°C.

We also subjected portions of typical boules to thermogravimetric determinations in argon, vacuum (10^{-6} bar), and ambient air. The samples showed no significant weight change during heating (5°C/min) to 1000°C in either argon or vacuum. In ambient air they showed no weight change up to 250°C, but on further heating began to oxidize at accelerating rates.

An advantage of the floating zone technique (Takei, 1978) is the avoidance of possible crystal contamination from a crucible material. However, we did not detect platinum in our fayalite (Table 3), and our crucible lifetime was usually >150 hours. Both techniques produce fayalite with comparable Fe^{3+} impurity levels at similar growth rates. However, under optimal conditions, the Czochralski method can yield boules which appear to have fewer of the banding and lineage effects described by Takei.

Role of Fe^{3+} in the growth of fayalite

There is uncertainty in the literature regarding the crystal chemistry and melting behavior of fayalite. Although natural samples frequently contain Fe^{3+} (*e.g.*, Yoder and Sahama, 1957), natural samples have also been found which are apparently Fe^{3+}-free (Burns, 1972). Bowen and Schairer (1932) reported that fayalite crystallizes from melts containing several weight percent Fe^{3+}, and whether Fe^{3+}-free fayalite can be crystallized from melts which probably contain considerable Fe^{3+} has been questioned (H. S. Yoder, personal communication, 1978). Bowen and Schairer concluded that ideally stoichiometric fayalite should melt incongruently and hence not crystallize from a melt of its own composition. Moreover, our boules are black in color, possibly due to $Fe^{2+} \rightleftarrows Fe^{3+}$ charge transfer processes (Wickersheim and Lefever, 1962); however, the band at 10,000Å

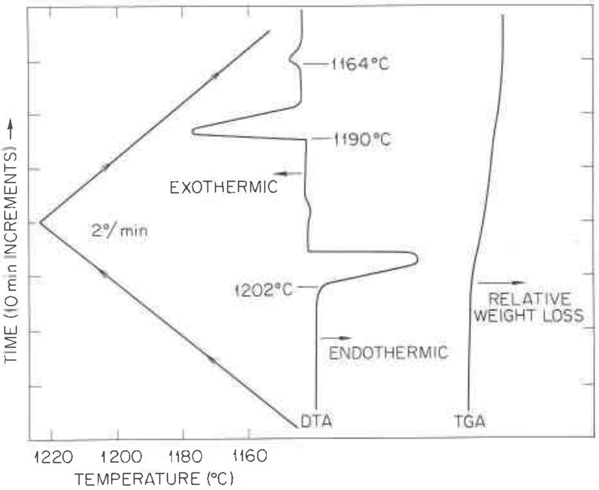

Fig. 6. Differential thermal and thermogravimetric curves for Czochralski-grown fayalite at $f(O_2) \approx 10^{-12}$ bar.

has been attributed to a *d–d* transition of Fe^{2+} alone (Burns, 1970).

Colorimetric data indicated crystal Fe^{3+} contents between 0.27% [$f(O_2) = 10^{-12}$ bar] and 0.86% [$f(O_2) = 10^{-9}$ bar], considerably less than the reported value of 1.8% for a melt in contact with Fe metal (Bowen and Schairer, 1932). The analysis of several fayalite samples by electron paramagnetic resonance at 77 K failed to detect Fe^{3+} (<10 ppm). We are unable to explain the inability of EPR to detect Fe^{3+} at the >1000 ppm level. The presence of significantly less magnetite in our boules than in the solidified melt suggests that Fe^{3+} is rejected to the melt under the growth conditions used. No attempt was made to determine the partition coefficient of Fe^{3+} between the boule and melt. The incorporation of Fe^{3+} might be greater in the presence of charge-compensating impurities (*e.g.*, Al^{3+}, Li^{+}), or at higher oxygen fugacities. Such factors could help explain the substantial amounts of Fe^{3+} often reported in natural olivines (Yoder and Sahama, 1957).

Applications

We conclude that it is possible to grow single crystals of fayalite under controlled conditions of $f(O_2)$, although it may not be possible to grow completely Fe^{3+}-free fayalite from a melt, even at the threshold of metallic iron formation. Homogeneous crystals grown under controlled conditions are needed because the amount of Fe^{3+} in fayalite can affect electrical conductivity (Sockel, 1973), optical absorption (Burns, 1972), magnetic susceptibility (Nitsan, 1974), dielectric loss (Morin *et al.*, 1978), and other properties.

The growth technique described should be useful in the preparation of other iron-bearing silicates, oxides, *etc.* The availability of such crystals should lead to a better understanding of the distribution of iron valence states and the influence that Fe^{3+}/Fe^{2+} exerts on significant crystal properties.

Acknowledgments

The authors thank O. B. Cavin (X-ray analyses), J. O. Thompson (Mössbauer), M. M. Abraham (EPR), J. P. Young (optical spectra), L. J. Brady (colorimetric analysis), L. A. Taylor (electron microprobe analysis), L. L. Hall (DTA/TGA), and C. F. Yen, M. T. Naney, L. A. Taylor, and R. J. Kirkpatrick (manuscript reviews). We are also indebted to T. J. Shankland and T. S. Usselman of the U.S. Geodynamics Single-Crystal Working Group, who ascertained the need for fayalite samples.

References

Bowen, N. L., and J. F. Schairer (1932) The system $FeO–SiO_2$. *Am. J. Sci., 24,* 177–213.

Burmeister, J. (1966) Czochralski growth of $Fe_{2-x}O$. *Materials Res. Bull., 1,* 17–26.

Burns, R. G. (1970) Crystal field spectra and evidence of cation ordering in olivine materials. *Am. Mineral., 55,* 1608–1632.

——— (1972) Cation determination curves for Mg–Fe–Mn olivines from vibrational spectra. *Am. Mineral., 57,* 967–985.

Deer, W. A., R. A. Howie and J. Zussman (1962) *Rock-forming Minerals,* Vol. 1. Wiley, New York.

Deines, P., R. H. Nafziger, G. C. Ulmer and E. Woermann (1974) Temperature–oxygen fugacity tables for selected gas mixtures in the system C–H–O at one atmosphere total pressure. *Bull. Earth and Mineral Sci. Experiment Station No. 88.*

Finch, C. B. and G. W. Clark (1971) Czochralski growth of single-crystal Mg_2SiO_4 (forsterite). *J. Cryst. Growth, 8,* 307–708.

——— and O. C. Kopp (1977) Czochralski growth of high-purity single-crystal fayalite (Fe_2SiO_4). *Metals and Ceramics Division Annual Progress Report, ORNL-5311.*

———, G. W. Clark and O. C. Kopp (1975) Growth of single-crystal Mn_2SiO_4 (tephroite) by Czochralski and edge-defined film-fed techniques. *J. Cryst. Growth, 29,* 269–272.

Fukao, Y., H. Nizutani and S. Uyeda (1968) Optical absorption spectra at high temperature and radiative thermal conductivity of olivines. *Phys. Earth Planet. Interiors, 1,* 57–62.

Ginley, D. S. and R. J. Baughman (1976) Preparation and Czochralski crystal growth of the iron titanates, $FeTiO_3$, Fe_2TiO_4 and Fe_2TiO_5. *Materials Res. Bull., 11,* 1539.

Hansen, M. (1958) *Constitution of Binary Alloys.* McGraw-Hill, New York.

Horn, F. H. (1961) Growth of single-crystal iron ferrites by the Czochralski method. *J. Appl. Phys., 32,* 900–901.

Laudise, R. A. (1970) *The Growth of Single Crystals.* Prentice-Hall, Englewood Cliffs, New Jersey.

Morin, F. J., R. M. Housley and J. R. Oliver (1968) Electrical properties of forsterite, *Trans. Am. Geophys. Union, 59,* 397.

Muan, A. (1965) Phase equilibria in the system $FeO–Fe_2O_3–SiO_2$. *Trans. AIME, 203,* 965–976.

Nitsan, U. (1974) Stability field of olivine with respect to oxidation and reduction. *J. Geophys. Res., 79,* 706–711.

Sockel, H. G. (1973) Defect structure and electrical conductivity of crystalline ferrous silicate. In M. M. Seltzer and R. I. Jaffie, Eds., *Defects and Transport in Oxides,* p. 341–355. Plenum Press, New York.

Takei, H. (1976) Czochralski growth of Mn_2SiO_4 single crystal and its properties. *J. Cryst. Growth, 34,* 125–131.

——— (1978) Growth of fayalite (Fe_2SiO_4) single crystals by the floating-zone method. *J. Cryst. Growth, 43,* 463–468.

Wickersheim, K. A. and R. A. Lefever (1962) Absorption spectra of iron-containing oxides. *J. Chem. Phys, 36(3),* 844.

Yoder, H. S. and Th. G. Sahama (1957) Olivine X-ray determination curve. *Am. Mineral., 42,* 475–491.

Manuscript received, July 20, 1979;
accepted for publication, November 24, 1979.