

Optical Floating Zone Growth of Single Crystal α -Fe₂O₃ from a CaFe₄O₇-Based Solvent

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ABSTRACT: Large single crystals (Φ 5 × L 33 mm) of hematite (α -Fe₂O₃) have been grown using a CaFe₄O₇-based solvent and 8 bar of oxygen in a four-mirror optical floating zone furnace in the traveling solvent zone configuration. The crystals grow along the [001] direction, are of excellent quality, and contain no residual Ca contamination from the solvent.

Introduction

Iron oxides are ubiquitous in aerosols, waters, soils, and sediments, and play an important role in global geochemical cycles.¹ In particular, interest in the mineral hematite (α -Fe₂O₃) is widespread, and a considerable body of work has focused on hematite's chemical and physical properties. Hematite's unique properties are also of interest in the study of catalysis, corrosion of iron, fluxes used in the production of steel, photoelectrolysis, dyes and stains, and magnetic recording media.

The properties of hematite are known to be sensitive to the type and concentration of impurities, preparation methodology, and thermal history.^{2,3} For example, naturally occurring and synthetic α -Fe₂O₃ have been reported to have differences in their magnetic properties.^{4,5} We have found that mineralogical samples often contain impurities that can vary among samples in type and amount. Spectroscopic as well as wet chemical methods have revealed the presence of impurities in over 15 different mineralogical samples.

For research purposes, single crystal samples are preferred and are often required to perform studies on a simplified model system. Large single crystals can be cut to present practically any crystallographic plane, allowing one surface (or direction) at a time to be studied, so that fundamental information can be obtained from an otherwise complex system. For example, in heterogeneous catalysis, differences in reactivity between two surfaces of the same material may be caused by differences in the geometrical configuration of atoms on the different crystallographic planes.⁶ From a practical standpoint, single-crystal samples also need to be large enough to facilitate mounting and manipulation in an analysis chamber. While thin film samples of hematite meet some of these requirements, there is often a need to mitigate the effects of a substrate and thermal history on these types of samples.

The synthesis of bulk single-crystal α -Fe₂O₃ has been reported using various techniques including sol-gel, hydrothermal, vapor transport, and flux methods. Crystals grown using sol-gel⁷ or hydrothermal methods⁸ are small, with an average grain size of typically a few microns. Likewise, crystals grown via vapor transport are typically small in size or exist only as thin platelets of [001] orientation.^{9,10} The disadvantage of thin platelets (of any size) is that their thin nature precludes obtaining samples of a different crystallographic orientation from a single specimen. Hematite growth by flux methods are reported as early as 1854, and an extensive review can be found in ref 11. Wanklyn and co-workers^{12,13} have systematically studied a variety of flux systems for the growth of single-crystal hematite; however, the resulting crystals were relatively small in size, basal plates or of variable and unpredictable orientation, or as in the case of any crystal grown using flux techniques, may contain material incorporated from the flux (impurity concentrations are not reported in many cases). Barks and Roy,¹⁴ employing a flux technique, were able to grow relatively pure large single crystals (averaging 0.1 atomic percent potassium and 10 mm in size) using a K₂B₄O₇ flux; however, these were thin basal-plane oriented platelets.

In contrast to the flux methods, growth in an optical floating zone furnace produces crystals that are large in three dimensions from which large samples of specific orientations can be obtained. This technique has been successfully employed to grow the related iron oxides Wustite (Fe_{1-x}O)¹⁵ and magnetite (Fe₃O₄)¹⁶ in atmospheres of N₂ and CO₂, respectively, to control the oxidation state of iron. Nonetheless, in each case the resulting crystals required post growth annealing to obtain the desired stoichiometry, as the oxidation state of iron is known to be extremely atmospherically sensitive.^{16,17} In this paper, we present the single-step growth of a large, extremely high purity, single-crystal rod of α -Fe₂O₃ using a hemicalcic ferrite (CaFe₄O₇)-based solvent in the optical floating zone furnace in the traveling solvent zone configuration.

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Experimental Details

Crystal Growth. The feed material was high purity α -Fe₂O₃ powder (Alfa Aesar, 99.998% pure). The solvent, CaFe₄O₇, was synthesized by calcining Fe₂O₃ (Alfa Aesar 99.998%) and CaO (Alfa Aesar 99.999%) in a 2:1 molar ratio in a platinum crucible in air at 970 °C for 24 h with several intermittent grindings. Both the feed and solvent materials were mixed with 10 vol % aqueous poly(vinyl alcohol) (Alfa Aesar 98–99%, hydrolyzed low molecular weight) to facilitate densification. It has been shown that the quality of the starting rods (density and uniformity, for example) directly influence the quality of the crystal grown in the optical floating zone furnace¹⁸ and that, in some cases, binder is needed to facilitate the formation of high quality rods. The rods were formed by packing the powder with binder in a cylindrical rubber sleeve 6 mm in diameter by 90 mm long, which was then evacuated, sealed, and hydrostatically pressed at 70 kPa. In contrast to the common methodology of forming a small solvent disk which is then attached to the support rod, in this study the entire support rod was formed from the solvent material. To form dense polycrystalline rods, the packed and pressed rods were sintered in air. The α -Fe₂O₃ feed rod was sintered at 1400 °C for 3 h and then at 1475 °C for an additional 3 h. The CaFe₄O₇ support rod was sintered at 1200 °C for 24 h, and PXRD showed it was a two-phase mixture of Fe₂O₃ and CaFe₂O₄, which is consistent with the fact that CaFe₄O₇ is not stable below 1170 °C.¹⁹ The feed rod was suspended from the upper shaft of the floating zone furnace using a platinum wire, while the support rod was rigidly affixed to the bottom shaft using steel wire. Growth was carried out in an optical image furnace (CSI FZ-T-10000-H-VI-VP, Crystal Systems, Inc., Japan) equipped with four 300 W Tungsten halide lamps focused by four polished elliptical mirrors. The growth rates ranged from 0.15 to 0.2 mm/h, and the rods were counter-rotated at 18 rpm to provide for thorough mixing of the solvent zone. An overpressure of 8 bar of oxygen was applied during crystal growth to prevent reduction (see Discussion).

Crystal Characterization. Phase identification was performed by powder X-ray diffraction (PXRD) using a Scintag XDS 2000 diffractometer, CuK α radiation, and a nickel filter at room temperature. Data were collected at 0.02°/1s at 10° < 2 θ < 80°. Transmission electron microscopy (TEM) analysis and Laue diffraction were employed to determine the growth direction and crystalline quality of the as-grown rod. To prepare a TEM size sample, the rod was sliced into 500-micron-thick wafers perpendicular to the growth direction. A 3-mm-diameter disk was cut from the center of each wafer and then mechanically thinned to 100 microns using SiC paper and then polished with 0.5-micron alumina paste. Next, the sample was mechanically dimpled to approximately 10 microns in the center and thinned to electron transparency (denoted by the presence of a small hole) by 5 keV Ar⁺ ions in a Gatan Precision Ion Polishing System (PIPS) operated at 20 μ A. TEM analysis was carried out on a Hitachi UHV-H9000 TEM equipped with a double tilt stage and operated at 300 kV. Purity of the crystals was examined by inductively coupled plasma-atomic emission spectroscopy (ICP-AES) on a Thermo Jarrell Ash Atomscan 25. Spatial chemical mapping was performed using a Princeton Gamma Tech X-ray detector on a Hitachi S-3500N VP scanning electron microscope (SEM) operated at 12 kV.

Results

Initial growth attempts were made with a feed rod composed of 99.8% pure α -Fe₂O₃ (Alfa Aesar). The crystal was grown at a rate of 0.15 mm h⁻¹ for approximately 205 h. The resulting crystal measured 4 mm in diameter by 31 mm in length (Figure 1). The smooth rod revealed the shiny gray luster characteristic of hematite and did not develop facets during the growth. Upon cutting, the crystal was determined to be

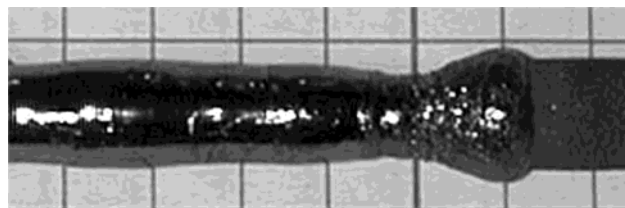


Figure 1. Synthetic polycrystalline hematite rod (left), from 99.8% pure starting material and 0.15 mm/h growth rate. Each line represents 5 mm. The CaFe₄O₇ support rod is to the right side, and only the first few millimeters are shown.

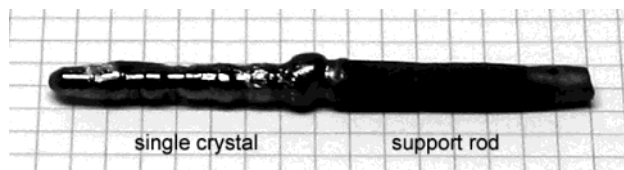


Figure 2. Synthetic single-crystal hematite rod, from 99.998% pure starting material and 0.2 mm/h growth rate. Each line represents 5 mm. The support rod is on the right-hand side, and the single crystal is to the left.

composed of small polycrystalline grains (3 mm² approximate grain size in cross section) at the beginning of the growth which coarsened to a very large grained polycrystal near the end of the growth. The largest single-crystal grain measured approximately 30 mm² in cross section and persisted for several millimeters along the length of the rod. Laue and TEM analysis of the large single-crystal grains revealed the [001] direction in the hematite corundum structure to be parallel to the rod growth direction. PXRD analysis confirmed the presence of α -Fe₂O₃ and no contaminating phases (Fe₃O₄, Fe_{1-x}O, CaFe₄O₇, etc.), while ICP-AES revealed the Ca/Fe ratio to be 0.005. There was no evidence of a Ca-rich second phase by optical microscopy, TEM, or EDX (spatial X-ray mapping), and it is therefore assumed that the CaO is in solid solution.

The highest quality and largest crystal was successfully grown using 99.998% pure α -Fe₂O₃ powder at a growth rate of 0.2 mm h⁻¹ for approximately 162 h (Figure 2). This rod measured approximately 5 mm in diameter by 33 mm in length. The total growth time was limited by the length of the feed rod prepared. Again, the crystal was determined to grow along the [001] direction by both Laue and TEM methods (Figure 3) and had the shiny gray luster characteristic of hematite. This crystal did not display any continuous faceting but did exhibit five rings where the diameter of the rod was larger and more constant than the other areas. While a change in operating conditions cannot be ruled out (lowering of the feed rod by the operator would cause more material to melt and hence increase the diameter of the growing rod), this may be due to facets presenting the r(1011) or n(2243), faces which are common beveling forms in hematite.²⁰ In this case, the entire rod was a single crystal (meaning no grain boundaries) except for the initial 3 mm of growth, which was polycrystalline. The Ca content of the as-grown crystal was below the detection limit of ICP-AES.

TEM analysis was performed on several representative samples of each of the crystals grown and revealed the crystalline quality of the rods to be excellent.

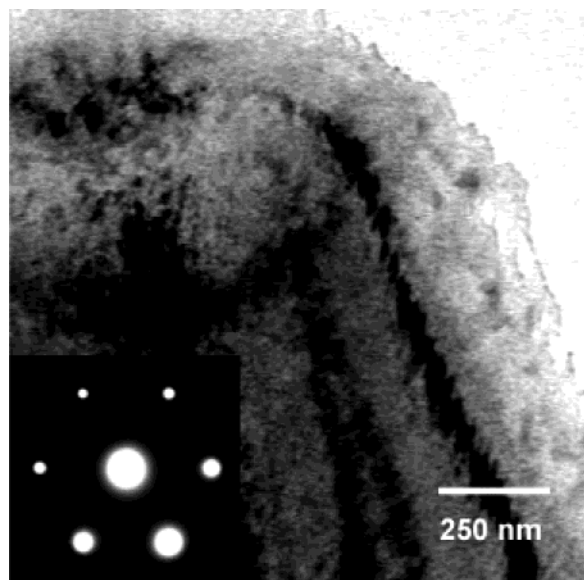


Figure 3. TEM bright-field image of Ar⁺ ion milled synthetic hematite showing bend (extinction) contours. [001] diffraction pattern (inset) demonstrates crystal growth along the *c*-axis in the hematite (corundum) structure.

Imaging (bright and dark field) as well as diffraction techniques did not provide any evidence of twinning, stacking faults, or dislocations in the as-grown crystal. In addition, there was no evidence of twinning, voids, inclusions, or cracks by optical microscopy.

Discussion

On the basis of the work of Kimura and Kitamura for the growth of single-crystal Fe₃O₄,¹⁶ the optical floating zone method has been shown to behave as a *closed system* for the preparation of iron oxides, meaning that the path of equilibrium crystallization follows the isopleth at the relevant composition. In the closed binary Fe–O system, hematite melts congruently to form liquid oxide at approximately 1575 °C.²¹ For a system of this type, one should be able to obtain hematite directly from a melt of equal composition.

Initial attempts to grow hematite directly from the melt at oxygen pressures ranging from atmospheric to 5 bar failed, as the samples reduced to magnetite and the accompanying oxygen release formed bubbles which destabilized the molten zone. Magnetite could be detected with a common magnet and was confirmed by PXRD. As expected the growth of hematite (in contrast to magnetite) from the melt in the optical floating zone furnace at moderate pressures behaves rather as an *open system*, where the path of equilibrium crystallization is constrained to follow the relevant oxygen isobar. To avoid the magnetite–hematite two-phase region of the binary phase diagram in an open system, pressures approaching 50 atm are needed²² to congruently melt and cool hematite directly. This reality is corroborated by the work of Balbashov et al.,²³ who demonstrated hematite growth directly from a melt of equal composition at oxygen pressures above 35 atm and in a specially modified floating zone furnace²⁴ which could accommodate the high pressure required. The maximum total pressure in the image furnace (Crystal Systems, Inc., Japan) is limited because the growth takes place inside

of a sealed quartz tube, which can safely hold approximately 9 bar of pressure when it is in good physical condition. In addition, the quartz tube is subject to devitrification when exposed to temperatures above 1150 °C. Devitrification, which can weaken the mechanical integrity of the tube, and therefore its ability to hold high gas pressures, can lead to failure and explosion. Thus, the furnace is equipped with a poppet valve which limits the attainable pressure to 9 bar; even so, the system should be monitored continually to ensure the integrity of the tube.

Considering these observations, we attempted to grow hematite employing a solvent which would form a stable liquid phase that would not reduce under the pressures safely attainable in the traveling solvent zone furnace. The use of a solvent in the optical floating zone furnace may seem like a contradiction because one of the main advantages of the system is that it is crucible free and therefore mitigates contamination. However, with the present configuration (meaning maximum attainable safe operating pressure of 8–9 bar), hematite cannot be directly grown from the melt.

To find a suitable solvent for use in an optical floating zone furnace, several additional considerations were taken into account compared to those for a flux assisted growth in a crucible. First, the solute and solvent must form a liquid phase with enough surface tension to sustain a molten floating zone between the two rods during the growth process.¹⁶ Preferably the solvent should not penetrate deeply into the feed rod by capillary action along grain boundaries, thereby causing an unstable growth condition. In addition, the solvent chosen must have a low vapor pressure in the liquid phase such that it will not evaporate during the course of the growth. If the solvent of choice was volatile and evaporated during the course of the growth, the liquid composition would change constantly and effect the establishment of the dynamic equilibrium needed for continuous growth of a crystal of constant composition. Early growth attempts using V₂O₅- and WO₃-based solvents failed because of severe penetration and solvent volatility, respectively.

Hematite was grown successfully using a hemicalcic ferrite (CaFe₄O₇)-based solvent which serves to both lower the temperature at which hematite solidifies from the melt compared to the binary Fe–O system and prevent hematite's reduction to magnetite. As mentioned previously, reduction to magnetite was observed in the Fe–O binary system at the growth conditions achievable in the optical floating zone furnace. CaFe₄O₇-based solvent was chosen because the Ca²⁺ ion (1.0 Å with 6-fold coordination) is larger than the ferric iron ion (with 6-fold coordination, 0.645 Å in the high spin configuration, 0.55 Å in the low spin configuration),²⁵ because CaO is nonvolatile in the temperature regimes used for single-crystal growth of hematite²¹ (the vapor pressure at 2337 °C is only 1.013 mbar²⁶), and because it lowers the temperature at which hematite solidifies from a melt by 350 °C compared to pure hematite.²⁷

CaFe₄O₇ (2Fe₂O₃·CaO) is a high-temperature phase which is metastable below 1170 °C. In the true binary system, CaFe₄O₇ undergoes a peritectic reaction at 1250 °C, decomposing to hematite and liquid. The two-phase mixture (hematite plus liquid) then melts to form a

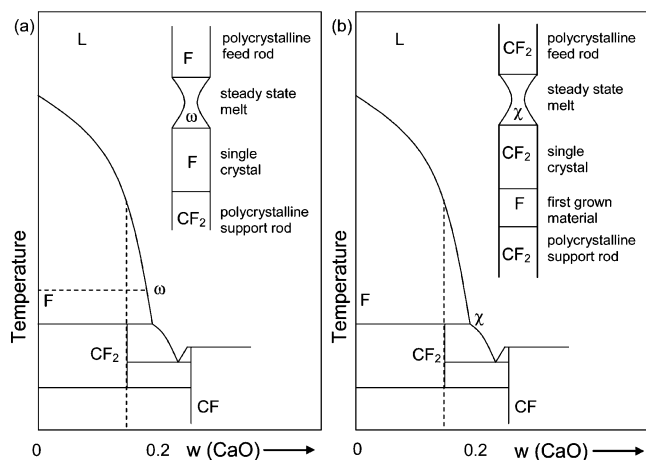


Figure 4. Schematic view (after refs 30 and 27) of crystal growth in a peritectic system. Keeping with the special notation used in describing these oxide systems, F denotes Fe_2O_3 , and C denotes CaO. It follows that CF_2 represents CaFe_4O_7 . (a) Growth of a congruently melting compound (F) from an incongruently melting compound (CF_2), analogous to the push–pull method. This is a schematic representation of the growth of Fe_2O_3 from the CaFe_4O_7 -based solvent. (b) Crystal growth of an incongruently melting compound. Upon cooling the melt, initially the first-grown material (F) is deposited. As zone leveling is established, the liquid composition reaches the peritectic point (ζ) as solid of the incongruently melting material (CF_2) is deposited. This is a schematic representation of the growth of CaFe_4O_7 from the melt.

single liquid phase of CaFe_4O_7 composition at approximately 1375 °C. Relating to single-crystal growth in the traveling solvent zone furnace, this means that once the top of the support (solvent) rod is fully melted and a liquid of CaFe_4O_7 composition is formed, hematite will nucleate onto the support rod because of the dynamic steady state and large temperature gradients present. As hematite is precipitated from the melt, and therefore to prevent so-called zone leveling²⁸ from occurring (in which the equilibrium would continue down the liquidus line to the peritectic point and establish a Ca-rich steady-state melt composition thereby depositing solid CaFe_4O_7), $\alpha\text{-Fe}_2\text{O}_3$ needs to be replenished via the feed rod to maintain a constant Fe-rich liquid composition. This is analogous to the “push–pull” method of single-crystal growth developed by Nelson for growth of germanium,²⁹ by which the liquid composition is held constant by continuously adding material (of the same composition) as the growing rod. If the equilibrium liquid composition at the solidification front remains Fe-rich, then only hematite, what is commonly known as the “first grown material”, will be deposited (Figure 4a). Note that this procedure is different from the case of other peritectic systems in which zone leveling and deposition of the incongruently melting phase are desired. In the case for growth of $\text{Mg}_3(\text{VO}_4)_2$,¹⁸ $\text{Y}_3\text{Fe}_5\text{O}_{12}$ - (YIG) ,¹⁶ and high T_c cuprates³⁰ for example, both the support (or solvent disk, as the case may be) and feed rods are composed of the incongruently melting material, and in these cases, zone leveling occurs, and after a brief period in which what is known as the first grown material is deposited, crystallization of the incongruently melting phase commences (Figure 4b). In fact, the optical floating zone furnace in the traveling solvent zone configuration is unique in its ability to handle such

peritectic phase transitions and grow single crystals of incongruently melting materials.

Experimentally there are several considerations to address in employing the CaFe_4O_7 -based solvent. First is that the $\text{CaO}\text{--}\text{Fe}_2\text{O}_3$ system is not a true binary system in realistically attainable pressure regimes. In fact, at 1 atm of O_2 there is a small magnetite (Fe_3O_4) and magnetite plus liquid stability region above 1400 °C and 0.93 wt % Fe.³¹ We have found that the formation of magnetite at any stage is detrimental to the single-crystal growth, because the resulting liberation of oxygen destabilizes the molten zone which cannot be recovered. Therefore, even though upon cooling any magnetite formed would transform to hematite according to the equilibrium phase diagram, growth in this regime must be avoided entirely. This can be accomplished by maintaining the oxygen pressure as high as safely attainable to minimize this magnetite phase regime, being careful in the initial stages of growth to melt only a small amount of the hematite feed rod (the amount of which will vary with the diameter of the rods and the growth rate), and by using the minimum power necessary in the heating lamps. Employing this solvent system and taking into account the above considerations, a stable molten zone was obtained, and the growth proceeded in the normal way; that is to say, the molten zone traveled along the length of the feed rod while $\alpha\text{-Fe}_2\text{O}_3$ crystallized onto the support rod from solution due to a dynamic steady state.

As mentioned above, to prevent reduction to magnetite and resulting release of gaseous oxygen, which destabilizes the molten zone, an overpressure of 8 bar O_2 was applied for the duration of the growth. The standard Viton seals at the top and bottom of the quartz tube in the imaging furnace had to be replaced with spring-in-cup seals to maintain this high pressure over the long time period (the floating zone furnace is not designed for elevated pressure). In this manner, the furnace was able to maintain the required pressure with only momentary fluctuations of less than 1 bar.

Additionally, we found that the successful growth of hematite at oxygen pressures near 8 bar in the optical floating zone furnace is directly dependent on when, in the start up procedure, that pressure is applied to the system. The stability of the molten zone and quality of the resulting crystal were found to be directly dependent on the pressure of oxygen inside the quartz tube. To prevent bubbling (release of gaseous oxygen accompanying a reduction of Fe^{3+} to Fe^{2+}), a pressure of approximately 6 bar must be applied before the lamps are turned on and melting of the support charge begins. When the furnace is pressurized in this manner, the molten zone is not reduced, yet the gas pressure in the furnace can accommodate the additional increase in pressure caused by the gas expansion upon heating. As soon as the CaFe_4O_7 support rod is melted, the balance of the pressure is applied and then the two rods are joined. When growth was attempted by first melting the rods in air and then applying the pressure, the molten zone was not stable, collapsed after several hours, and could not be reformed again as the flux had flowed down the edge of the support rod.

Conclusion

We have presented the results from a single-step growth of large single-crystal α -Fe₂O₃ by the optical floating zone method in the traveling solvent zone configuration using a hemicalcic ferrite-based solvent. The best single crystals measure nominally 5 mm in diameter by 33 mm in length and contain no residual Ca contamination from the flux as evidenced by ICP-AES. TEM and Laue analysis reveal the growth direction to be parallel to [001] and the crystalline quality to be excellent.

It should be noted that using the optical floating zone furnace in the traveling solvent zone configuration with this type of flux system is a new methodology for growing single crystals of atmospherically sensitive materials. Unique to the growth of hematite, we have used the peritectic reaction to our benefit in thermally decomposing an incongruently melting material to grow a large single crystal of an entirely different phase. There is no solvent that exists in the binary Fe–O system. As previously mentioned, in contrast to the quite common method of employing a solvent from within the system of interest (for example, in the case of YIG³² and high *T_c* cuprates³³), we have used a solvent that contains a species which is wholly undesirable in the final product. While this is not the first time that a foreign species has been introduced as a solvent in this type of furnace configuration, it is the first time that it has been used in this way and resulted in a 100% pure, entirely single-crystal rod in a single-step growth which required no post-growth annealing. ZnO was grown in the optical floating zone furnace using V₂O₅+B₂O₃ and V₂O₅+MoO₃ fluxes;³⁴ however, the growth required the “twice scanning technique”. In addition, the as-grown ZnO contained residual V or Mo and was polycrystalline.

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Supporting Information Available: Photographs of the optical floating zone furnace. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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