Identification of Gravity-Related Effects on Crystal Growth from Melts with an Immiscibility Gap

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1. Introduction and Objective

This work involves an experimental-numerical approach to study the effects of natural and Marangoni convections on solidification of single crystals from a silicate melt with a liquid-liquid immiscibility gap. Industrial use of crystals grown from silicate melts is becoming increasingly important in electronic, optical, and high temperature structural applications. Even the simplest silicate systems like Al_2O_3-SiO_2 have had, and will continue to have, a significant role in the development of traditional and advanced ceramics. A unique feature of crystals grown from the silicate systems is their outstanding linear electro-optic properties. They also exhibit exceptionally high optical rotativity. As a result, these crystals are attractive materials for dielectric, optical, and microwave applications.

Experimental work in our laboratory has indicated that directional solidification of a single crystal mullite appears to be preceded by liquid-liquid phase separation in the melt. Disruption of the immiscible state results in crystallization of a two phase structure. There is also evidence that mixing in the melt caused by density-driven convection can significantly affect the stability of the immiscible liquid layers and result in poly-crystalline growth. On earth, the immiscible state has only been observed for small diameter crystals grown in float zone systems where natural convection is almost negligible. Therefore, it is anticipated that growth of large single crystals from silicate melts would benefit from microgravity conditions because of the reduction of the natural convective mixing. The main objective of this research is to determine the effects of transport processes on the phase separation in the melt during growth of a single crystal while addressing the following issues:

1. When do the immiscible layers form and are they real?
2. What are the main physical characteristics of the immiscible liquids?
3. How mixing by natural or Marangoni convection affects the stability of the phase separated melt?

2. Background

Very little work has been done or published with regard to solidification from immiscible liquids. High resolution digital images obtained in our laboratories at NASA Lewis demonstrate that mullite formation is preceded by a state of liquid-liquid immiscibility. To our knowledge, this is the first direct experimental evidence of liquid immiscibility reported for this system. Experimental results also reveal that mixing in the melt caused by density-driven convection can significantly affect the growth process. The transport processes affecting concentration and temperature gradients in the melt and in the growing solid are quite complicated for the silicate systems. The immiscibility of the liquid, segregation of dopant, and interface shape are not only directly affected by density-driven and surface-tension-driven convection in the melt but are also indirectly influenced by a significant amount of radiation and conduction heat transfer through the semi-transparent solid. The interaction between the various transport processes are further complicated by the observed multi-layered fluid structure which brings about various mechanical and thermal couplings across the liquid-liquid interface. Consequently, determination of the necessary conditions for growing superior quality single crystals from phase separated melts is not an easy task and requires isolating the effects of the various interacting transport processes using a combined experiments and numerical modelling approach.
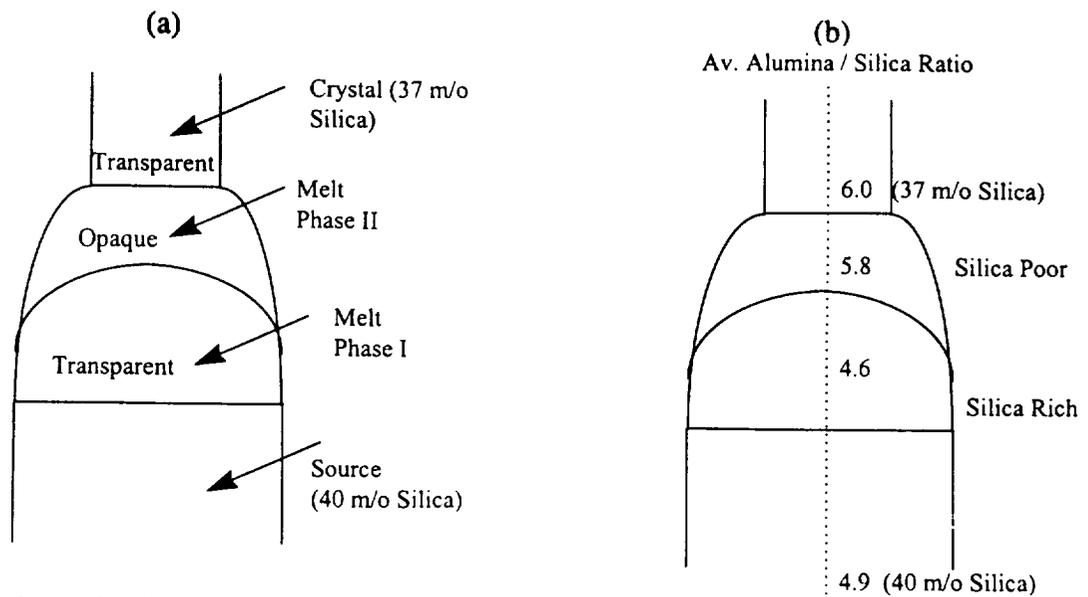
(a)

Crystal (37 m/o Silica)

Transparent

Melt Phase II

Opaque

Melt Phase I

Transparent

Source (40 m/o Silica)

(b)

Av. Alumina / Silica Ratio

6.0 (37 m/o Silica)

5.8   Silica Poor

4.6

Silica Rich

4.9 (40 m/o Silica)

Fig. 1 a) Schematic of Phase-Separated Melt in The Float Zone Setup, and b) Qualitative Alumina/Silica Concentration Map.

3. Results and Discussion

As a first step towards gaining the necessary insight into the physical phenomena governing growth of mullites from melt, a series of tests were performed to determine the physical nature and characteristics of the melt during growth. The growth set up consists of a CO_2-laser heated float zone apparatus with operational temperatures around 1800-2200. The melting temperature of the mullite is around 1850 °C and crystal are pulled in an air atmosphere with no rotation of the crystal or source material.

Observation of Liquid-Liquid Immiscibility: Solidification experiments demonstrate that during growth of a single crystal mullite from a source material with a composition of about 33 m/o, the melt separates into two distinct phases as sketched in Fig. 1a. High resolution digital images of the melt as shown in Figs. 2 and 3 indicate that the Phase-II liquid adjacent to the crystal is less transparent to visible light than the Phase-I liquid in the interior of the melt next to the source. Optical micrographs of the cross section of the quenched molten zone also confirm the visual images by indicating a distinct difference between the scattering intensity and refractive indices of the two melt regions. The immiscibility may be brought about by structural and/or compositional differences in the melt.

Characteristics of The Two Liquid Layers: Anecdotal evidence suggests that the domed transparent Phase I liquid next to the source has a much larger viscosity than the Phase-II liquid next to the growing crystal. A qualitative map of alumina/silica concentration of the quenched solid was developed through energy disbursive spectroscopy using a field emission Hitachi SEM. The results reproduced in Fig. 2b provide a qualitative measure of the change in alumina/silica concentration through the ratio of their respective characteristic x-ray peak integrals. According to these measurements the Phase I liquid is enriched in silica as compared to the Phase-II liquid and the source.

Poly-crystalline Growth: Our numerous experimental runs suggest that phase separation in the melt is a necessary but insufficient condition for growth of a single crystal. Single crystal growth occurs at melt temperature levels around 2015 °C for small diameter (100 microns) crystals. But at lower melt temperature levels and larger diameters poly-crystalline growth prevails with a rough domed shaped interface protruding into the melt as shown in Fig. 4. SEM micrographs of the single crystal and the poly-crystalline solid are included in Fig 5. Note that poly-crystalline growth results in a solid composed of mullite with alumina-silicate glass at the grain boundaries

Seeding Experiments: A series of experiments were also performed using alumina, silica and mullite seeds to determine the effect of seeding on the liquid-liquid phase separation in the melt. When alumina seeds were used, the Phase-II liquid layer formed rapidly next to the crystal at tem-

— Single Crystal
Mullite

— Solidification
Interface

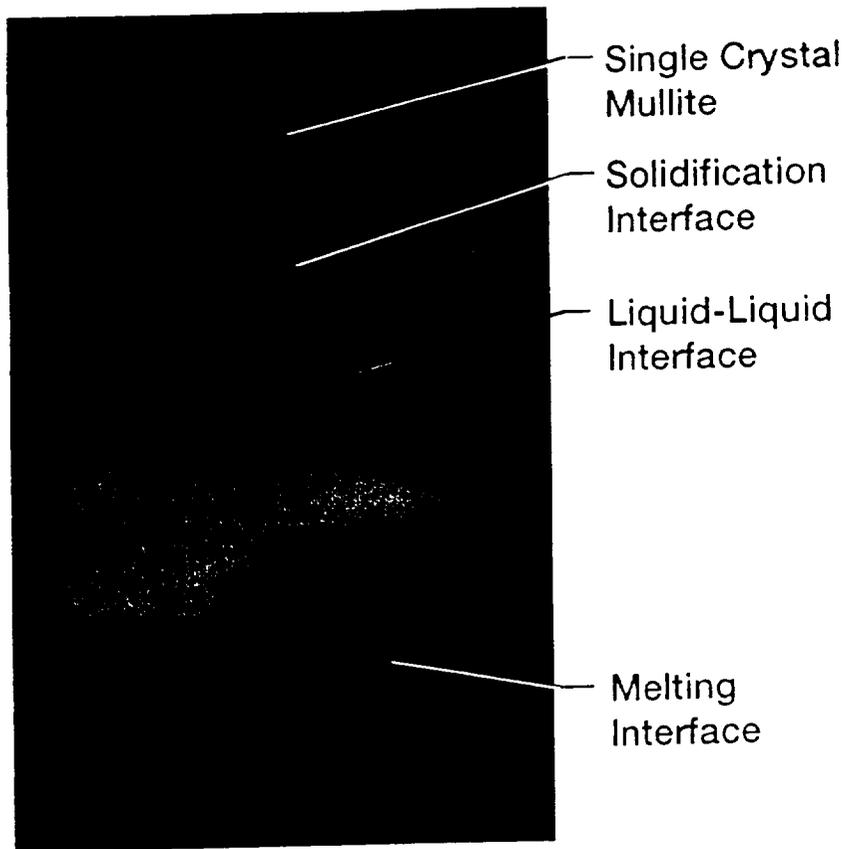— Liquid-Liquid
Interface

— Melting
Interface

Fig. 2   High Resolution Digital Images Captured During Mullite Crystal Growth
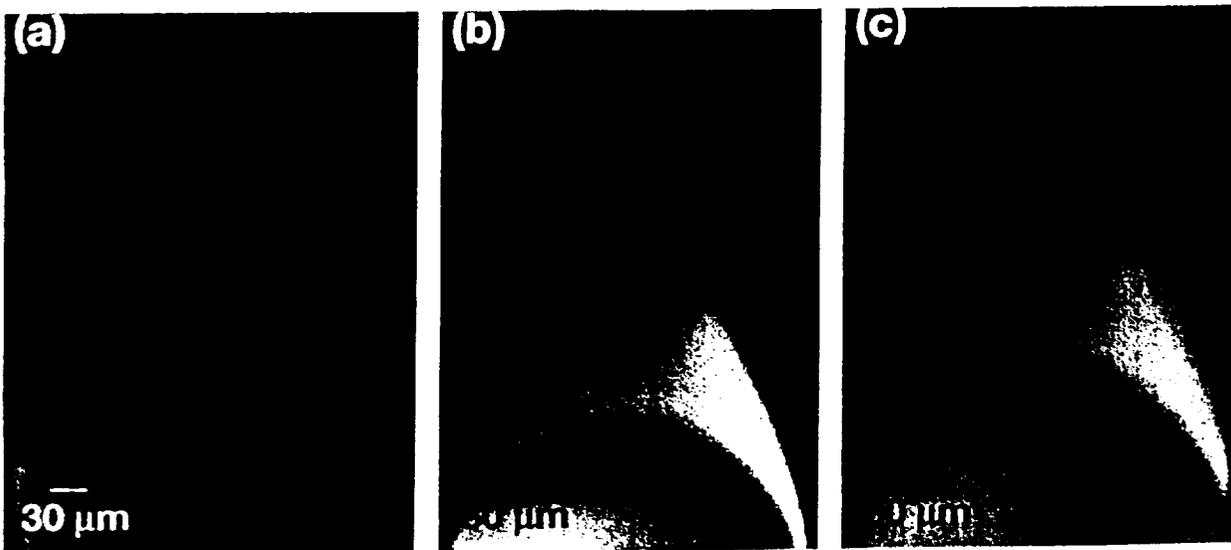

Fig. 3 a) Initiation of Single Crystal Growth, b) Subsequent Occurrence of Large Facets, c) Non-centro-symmetric Position of Crystal Fiber Relative to Melt as a Result of Faceted Growth.
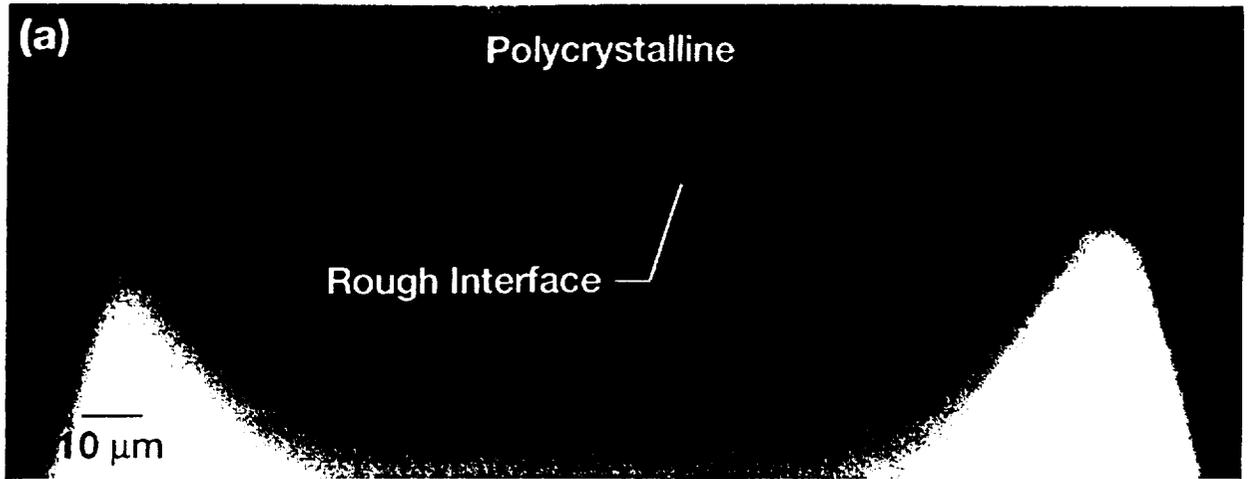
Fig. 4 High Resolution Digital Image of a Rough Domed Liquid-Solid Interface in a Poly-Crystalline Growth.
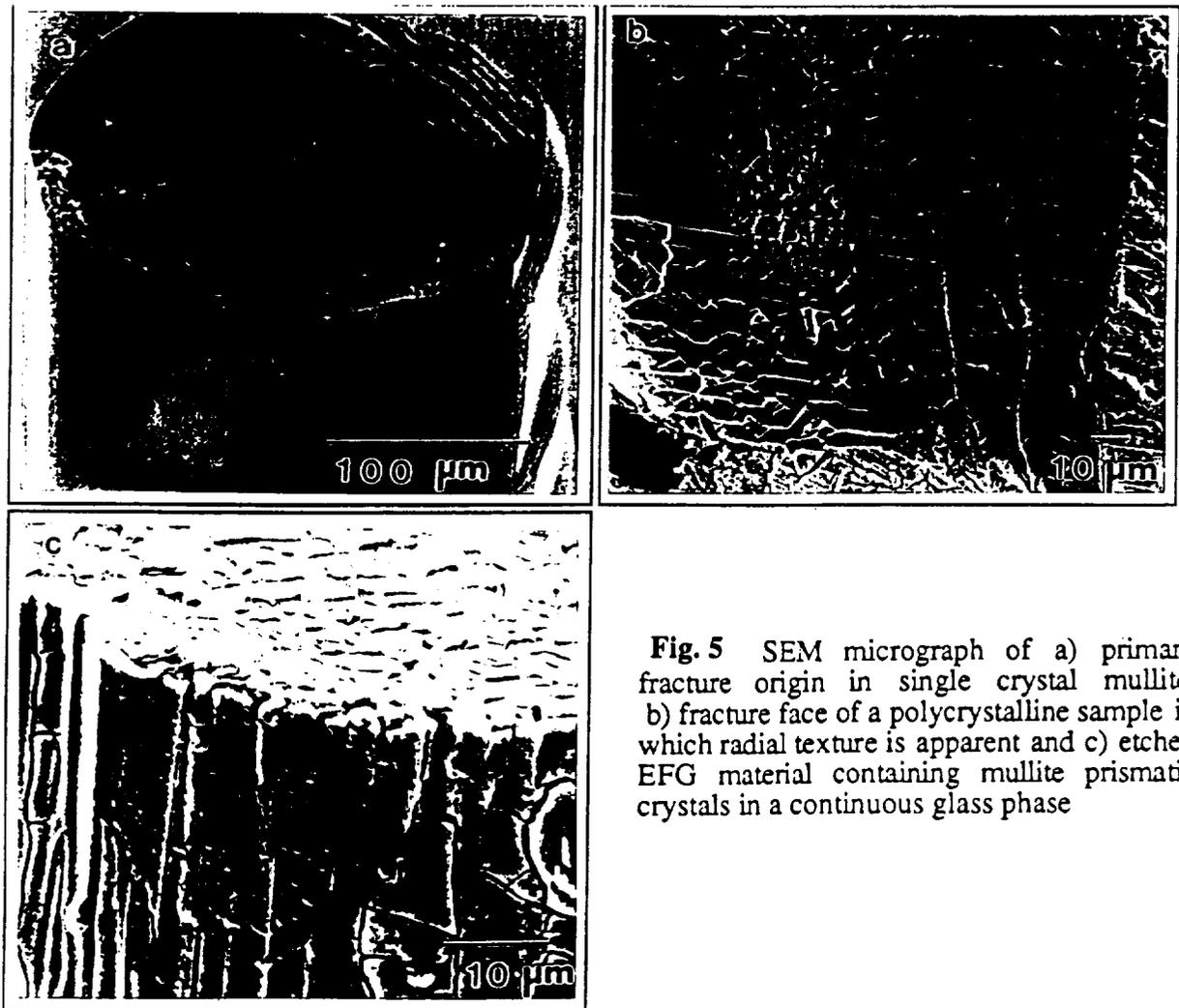

Fig. 5 SEM micrograph of a) primary fracture origin in single crystal mullite, b) fracture face of a polycrystalline sample in which radial texture is apparent and c) etched EFG material containing mullite prismatic crystals in a continuous glass phase
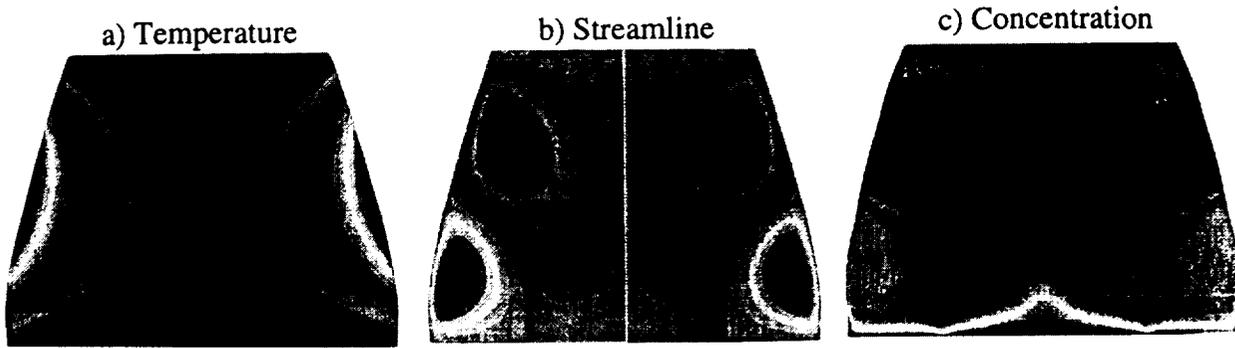
Fig. 6 a) Temperature, b) Flow, and c) Concentration Fields for a Thermocapillary Convection Dominated Case (Ma = 2.4, Ra, $2,4(10)^{-4}$, Pr=10, Sc=10,000).

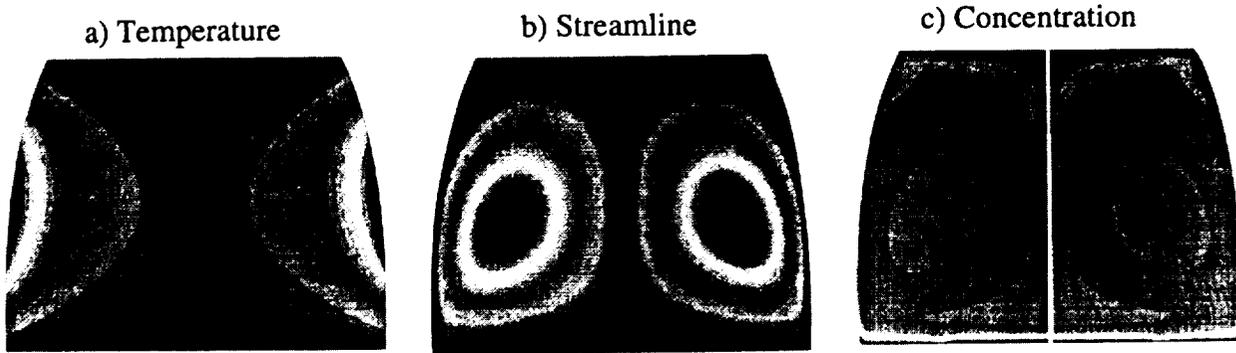**Fig. 7**a) Temperature, b) Flow, and c) Concentration Fields for a Natural Convection Dominated Case (Ma = 2.4, Ra, 24., Pr=10, Sc=10,000).

perature levels around 1850 °C. When silica seed was used, the liquid-liquid phase separation did not readily take place. This might be due to excess silica in the melt. Nevertheless, It was possible to promote phase separation in two ways; either by increasing melt temperature levels or by tolerating long periods of poly-crystalline growth. It is believed that in the former case excess silica is removed by an increased evaporation rate and in the latter case excess silica is removed as the grain boundary phase. Finally, in tests with the mullite seed liquid-liquid phase separation occurred more readily compared to silica seeding but not as easily compared to alumina seeding.

Role of Transport Processes: It seems that successful growth of single crystal mullite requires a specific level of alumina concentration near the interface which in the float zone setup is determined by a dynamic balance between:

1. Evaporation of silica at the gas-melt interface
2. Rejection of silica at the crystal-melt interface
3. Transport of alumina through the phase-separated melt layers

This balance is sensitive to variations in the temperature level in the melt which controls the evaporation, diffusion, and convection rates and to variations in the melt diameter which is determines the dominant mode of convection and controls the intensity of mixing in the melt.

At small crystal diameters grown by the float zone technique, convection is not strong enough to affect the temperature field. Therefore, conduction is dominant in the melt. Radiation of course is the main heating mechanism due to the laser heating of the melt and also the main heat loss mechanism through the semitransparent crystal. There is also heat of evaporation at the gas-melt interface due to silica evaporation which is not easily quantifiable. At small diameters, Marangoni (thermocapillary) convection is dominant giving rise to concentrated vortices near the gas-melt interface which bring about only localized mixing. But at larger diameters, natural convection becomes dominant giving rise to a strong bulk flow which causes vigorous bulk mixing in the melt. Species transport takes place by convection and diffusion. Diffusion across the liquid-liquid interface is important, but at Schmidt numbers around 10,000, convection can easily modify the con-

centration profiles. Evaporation of silica at the melt-gas interface and rejection of silica at the melt-crystal interface have also considerable effects on the species distribution.

Numerical Simulations: A Finite element model was developed to simulate the transport processes in the float zone setup. Currently, the model includes heat, momentum, and species transport. Effects of natural and Marangoni convection, laser heating, silica rejection at the crystal-melt interface and silica evaporation at the melt-gas interface are all included. The gas-liquid interface is treated as a free surface the shape of which is determined by a force balance during the simulation. Future extensions of the model will include a rigorous formulation for the phase-separated melt and for the radiation transfer through the semi-transparent crystal.

Numerical simulations of the temperature, flow and concentration fields for the small diameter case which is dominated by thermocapillary convection are shown in Fig. 6a-c. The temperature field in Fig 6a indicates that the hottest spot occurs near the middle of the gas-melt surface where the laser beam is directed at. Transport of heat in the melt is by conduction and the resulting flow is not strong enough to modify the temperature pattern. This results in a relatively cold core in the center of the melt. At small diameters, natural convection effects are minimal and thermocapillary convection is dominant. Because the thermal coefficient of surface tension for the mullite melt is positive, the thermocapillary flow occurs from the cold region near the crystal melt interface towards the hot spot on the surface giving rise to a four-vortexed cellular pattern which provides localized mixing near the melt-gas interface as indicated in Fig. 6b. This mixing is not strong enough to affect the temperature field because of the relatively low Prandtl number, but strong enough to modify the concentration field as shown in Fig. 6c because of the large Schmidt number for the mullite melt.

Numerical simulations of the temperature, flow, and concentration fields for a larger diameter case are shown in Fig. 7a-c. This time, the flow is dominated by natural convection which results in a large buoyancy-driven vortex providing vigorous mixing in the bulk of the fluid as shown in Fig. 7b. As a result, the bottom thermocapillary vortex is completely wiped out and the top thermocapillary vortex is squeezed into a small region near the interface by the strong natural convective flow. Although the flow is not strong enough to modify the conduction dominated temperature field as indicated by comparing Figs 6a and 7a, it is strong enough to modify the concentration field drastically in the entire melt as evident in Fig. 7c. Results in Fig. 6 and 7, therefore, suggest that the relative strength of the thermocapillary to natural convection which is controlled by the ratio of the Marangoni to Raleigh numbers plays an important role in determining the flow structure in the melt.

4. Conclusion

Growth of single crystal mullite is preceded by liquid-liquid phase separation in the melt. Comparison of the numerically predicted concentration fields to the experimental measurements of the alumina/silica ratio and digital images of the phase separated melt suggests that the phase separation occurs because of structural differences. Our experiments have indicated that phase separation is a necessary but insufficient condition for single crystal growth. It seems that the phase separation is not considerably affected by the seeding material, but melt temperature levels and melt diameter play important roles by controlling the diffusion and evaporation of silica and the relative strengths of the thermocapillary and natural convection flows during growth.

Numerical simulations show that different convection patterns can prevail in the melt depending on the Raleigh to Marangoni number ratios. When natural convection is dominant, there is extensive mixing in the bulk of the melt which does not affect the temperature field noticeably but modifies the concentration fields significantly. This vigorous mixing might be responsible for the disruption of the layered melt structure at large diameters. To confirm these findings rigorously, work is underway to use an energy-based phase field method. The phase field approach together with the Navier Stokes equations provides a continuum surface tension model that can be used to focus on the interactions between the multi-layered fluid system created by the liquid-liquid immiscibility gap in the melt.