CHAPTER 4: GROWING SINGLE CRYSTALS

CERAMIC PROCESSING (MATR4350)

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WHAT IS A SINGLE CRYSTAL CERAMIC?

- single crystal, any solid object in which an orderly three-dimensional arrangement of the atoms, ions, or molecules is repeated throughout the entire volume.
- single-crystal, or monocrystalline, solid is a material in which the crystal lattice of the entire sample is continuous and unbroken to the edges of the sample, with no grain boundaries.
- Single crystals are one of the most important groups of materials due to their continuous, uniform, and highlyordered structure which enables them to possess unique properties.
- In many aspects, single crystal materials can be found to be advantageous over polycrystalline materials, and many properties which are found in single crystals cannot be replicated in polycrystals
- Even with the technological developments of advanced polycrystalline materials which are designed for specifc applications, the electrical, optical, thermal, mechanical, and other properties of single crystals still remain superior

WHAT ARE EXAMPLES OF SINGLE CRYSTALS?

- Single crystals of quartz, salt, Iceland spar, diamond, and topaz are examples of faceted natural single crystals.
- Polycrystals and polycrystalline aggregates, which consist of a set of small single crystals of various orientation, are distinguished from single crystals.
- Single crystals have found extensive use in optical, electronic, optoelectronic, and other applications.
- Due to their outstanding optical and electronic properties, single crystals of III–V semiconductors (GaAs, GaN) are an integral part of devices for application in fber-optic communication, wireless and satellite communication, solid-state lighting.
- The importance of single crystal alumina (sapphire) , as well as yttrium aluminum garnet (YAG), for laser materials has also been demonstrated through numerous applications.

WHAT IS SINGLE CRYSTAL GROWTH?

- Conventional techniques of single crystal growth

- 3 general approaches for the growth of bulk inorganic single crystals:
  - growth from melt, solution and vapor phase.
  - Growth from melt is the most commonly used method and is based upon the solidification and crystallization of a melted material

METHODS FOR GROWING SINGLE CRYSTALS OF CERAMIC

- The growth of single crystals involves one of the following changes of state
  - Liquid (pure or solution) →solid
  - Gas → Solid
- The atomic or molecular species in a fluid are, on average, arranged randomly.
- During crystal growth, they must move to the correct sites in the ordered structure of the crystalline phase.
- If crystal growth is too rapid, disordered regions (crystal lattice defects, such as dislocations) are trapped in the crystal or many smaller crystals with varying orientations are nucleated, thereby destroying the desired single-crystal perfection.
- The growth process involved in producing a single crystal must therefore be slow, and it requires precise control over the growth conditions (e.g., temperature) for prolonged periods.

- Several different methods are used commercially to grow single crystals.
  - can be divided into melt, solution, and vapor-phase techniques
- The operating cost does not include the cost of labor; the skill refers only to the difficulty in using the equipment, not in developing the process.
- The crystal perfection assumes the optimum conditions
  - the rate of flux growth depends on the complexity of the reaction
- The method chosen depends on the type of crystal, the application for that crystal, and the required size.
- The most widely used growth technique is the Czochralski (or Cz) process → it can produce very large dislocation-free crystals of silicon.

TABLE 29.2 Factors Relevant to the Choice of a Growth Technique for Crystal Production

	Equipment investment	*Operating costs*	*Skill needed*	*Development needed*	*Range of materials*	*Growth rate*	*Crystal perfection*
Cz	High	Medium	Medium	Medium	Many	Rapid	High
Bridgman	Low	Medium	Low	Little	Many	Medium	Medium
Verneuil	Medium	Low	High	Little	Some	Rapid	Low
Skull melting	High	Medium	Medium	Medium	Some	Rapid	Medium
Flux	Medium	Medium	Low	Much	Few	Slow	Variable
Hydrothermal	Very high	High	Medium	Much	Few	Slow	Variable
UHP	Very high	High	High	Much	Few	Slow	Variable
Gas phase	Low	Low	Low	Varies	Few	Very slow	Variable

METHODS FOR GROWING SINGLE CRYSTALS OF CERAMIC

MELT

- verneuil(flame fusion)
- arc image growth
- Czochralski (or Cz)
- skull melting
- Bridgman-stockbarger,
- HEM

SOLUTION

- hydrothermal
- hydrothermal growth at low temperature
- flux growth
- growing diamonds

VAPOR-PHASE

- VLS
- sublimation
- UHP

MELT-GROWTH TECHNIQUES

- Growth from melt is the most commonly used method →based on solidification & crystallization of a melted material.
- The Czochralski and Bridgman methods are the 2 most utilized melt-growth techniques.
- The Czochralski method (Cz) →very important for the production of single crystals for electronic & optical applications (silicon and germanium single crystals, fluoride and oxide single crystals)
- Single crystal growth from melt allows for the fabrication of large single crystals of excellent quality in a relatively short time when compared to other growth techniques
- Difficulties of melt growth:
  - In maintaining a stable temperature during the crystal growth
  - In achieving very high melting points for some materials
  - In achieving chemical homogeneity → when multiple elements are present in the system, reactivity of the melted material with the crucible
  - High costs of production and equipment

SOLUTION-GROWTH TECHNIQUE

- Solution-growth technique involves the dissolution of the material to be crystallized within a suitable solvent or flux (PbO, PbF_2, Bi_2O_3, Li_2O, Na_2O, K_2O, KF, P_2O_5)
- High-temperature solution growth (flux-growth)→ has been the most utilized technique for the fabrication of single crystals
  - convenient for materials that inconsistent melt or when melt-growth techniques cannot be applied.
  - Advantage → The crystals are grown below their melting temperatures & the growth of the crystal occurs spontaneously through nucleation/crystallization on a seed.
  - The crystal growth rates for the solution-growth method are much slower than that of the melt-growth method & the presence of flux ions is unavoidable in the crystal.
  - Growth of single crystals via the flux method has found many important applications in the production of single crystal materials (garnets, various laser crystals, including borates-$LiNbO_3$, $BaTiO_3$, BaB_2O_4) and more complex systems ($Sr_{1-x}Ba_xNb_2O_6$, $Pb_{1-x}Ba_xNb_2O_6$)

VAPOR-PHASE GROWTH TECHNIQUES

- Vapor-phase growth is more commonly applied to the fabrication of thin single crystals films on substrates than bulk single crystals.
- The growth of single crystals through the vapor phase can be accomplished via a sublimation process
  - reaction in the gas phase and transport reaction, such in the case of chemical vapor transport (CVT) and, physical vapor transport (PVT)
- Advantage → the vapor growth method utilizes lower processing temperatures which result in a significantly higher quality crystal due to avoidance of incorporating impurities, structural and compositional uniformities, and phase transitions.
- Drawback → the low growth and transport rates in the vapor to the interface, associated with the low temperature.
- This technique is still used if neither one of the other two techniques is applicable for the growth of single crystals → SiC single crystals

NEW TECHNIQUE FOR SINGLE CRYSTAL FABRICATION

- Another pathway for growing single crystals is through the solid-state conversion of polycrystalline materials to single crystals.
- This method is based on a phenomenon which can be observed in many systems→ abnormal grain growth (AGG).
- Solid-state single crystal growth was first observed and studied in metals as a possible alternative to very difficult and expensive procedures used to fabricate metal single crystals.
- Drawback of conventional single crystal growth techniques:
  - heating at high temperatures, maintaining compositional uniformity, contamination from the crucibles, were avoided during the solid-state single crystal growth and performed with much lower production costs.
- Due to considerable advancements made in nanotechnologies & sintering technology that have enabled the fabrication of high-quality ceramics, interest in solid-state single crystal growth from polycrystals has been renewed.
- Solid-state single crystal growth has been shown to be an efective and simple technique for obtaining single crystals with lower capital costs associated with production equipment and components, which could potentially allow for the mass production of single crystals for various existing as well as new applications

NEW TECHNIQUE FOR SINGLE CRYSTAL FABRICATION

- The technique utilizes conventional sintering equipment, such as simple furnaces, which cost notably less than the equipment for conventional single crystal growth.
- Furthermore, the more complex the composition is, the harder it becomes to fabricate a single crystal using the conventional single crystal growth route, due to chemical inhomogeneities, the presence of elements that melt incongruently, volatility of certain elements
- Solid-state single crystal growth has been found to be promising and applicable to many different systems, especially systems with complex chemical compositions.
- Advantages:
  - Net-shape production, when compared to cutting and shaping from the single crystal boules grown conventionally
  - cost-effectiveness of single crystals produced by solid-state growth since it reduces the number of machining steps after the growth process
  - even allows for growth of more complexly-shaped single crystals.

SOLID-STATE CONVERSION OF SINGLE CRYSTALS FROM POLYCRYSTALS

- In recent years, solid-state single crystal growth (SSCG) has emerged as a promising alternative technique for growth of single crystals through a conversion process in polycrystalline materials.
- This technique offers numerous advantages over conventional single crystal growth techniques, is based on the occurrence of AGG in polycrystals.
- SSCG technique is developed based on a “mixed control mechanism” of grain boundary migration as well as principles of microstructural evolution.
- The mixed control mechanism can be used as a general guiding principle for suppressing growth and controlling the growth of single crystals from polycrystalline materials, which are the key requirements for SSCG.

CHAPTER SUMMARY

- Many methods can be used to grow single crystals of ceramic materials.
- To produce large crystals, the methods can be classified as melt growth, solution growth, or vapor growth.
- Solution growth requires that a suitable solvent can be found for the material.
  - Because it is possible to find a solvent for most materials, solution-growth techniques are applicable to a very wide range of ceramics.
- Meltgrowth techniques generally require that the material melts congruently/nearly congruently
  - so knowledge of the phase diagram for the material is important.
  - This fact alone eliminates many materials from consideration.
  - The significant advantage of melt-growth techniques → Cz method- very high quality crystals can be produced.
- Vapor growth is generally used only for producing single crystal of ceramics (SiC) that can’t be made by either melt or solution techniques or for growing crystals.
- Many of the methods used for thin-film growth are producing single crystals

ASSIGNMENT 2

Describes and outlines 2 methods for growing single crystals of ceramics in slide presentation:

- Melt Technique: Verneuil (Flame-Fusion) & Arc-Image Growth – Haziq
- Melt Technique: Czochralski & skull Melting-Hazwan
- Melt Technique: Bridgman-Stockbarger & HEM -Naqib
- Solution Technique: Hydrothermal & Hydrothermal Growth at Low Temperature - Nazrin
- Solution Technique: Flux Growth & Growing Diamonds -Izzah
- Vapor Technique: VLS & Sublimation-Juliana