How to fast grow large-size crystals?

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ORIGIN AND COMPLEXITY

Large-size crystals are irreplaceable in such fields as semiconductors, communication, the military, and radiation detection. However, it is still very difficult to prepare large-size, high-quality single crystals with a fast-growing rate and low cost. "How to make breakthrough in the preparation theory and technology of large-size crystals" is one of the top ten challenges for science and technology released by the China Association for Science and Technology in 2021. The research on crystal growth has a long history of about 130 years, and many advances in both theoretical models and growth experiments have been made in this journey. In practice, crystal growth is a complicated process with multi-scale and multi-field properties, as shown in Figure 1. Multi-scale means that crystal growth involves issues of different levels such as occupied state of electrons, type of atoms/molecules, structure of clusters (mesoscopic scale), and properties of bulk (macro scale). Multi-field means the mutual coupling of electromagnetic, thermal, fluid field, and any other field that affects the crystal growth. Fortunately, with the rapid development and widespread application of artificial intelligence, breakthroughs for fast and large-size crystal growth are being anticipated in the near future. Here, on the foundation of our recent research and findings on the fast growth of large-size crystals, we present our answer.

MULTI-SCALE RESEARCHES

At the atomic or molecular scales, huge progress has been made in recent studies, shedding light on the microscopic mechanisms of large-size crystal growth. Fast growth of single crystals is affected by both kinetics and thermodynamics factors. Growth rate of crystals can be expressed as $V(T) = K(T)(1 - e^{-\Delta\mu/k_B T})$, where $K(T)$ represents the kinetic factor, and the items in the parentheses represent thermodynamic factors. Wilson and Frenkel proposed the WF model for crystal growth.[1] This model indicates that the diffusion of atoms is dominant in the micro-dynamic process of crystal growth, and it explains the decreasing of crystal growth rate with decrease in temperature. However, employing computational simulation methods, Broughton et al. found that the crystal growth rate could not be well predicted by the WF model during the solidification of the Lennard-Jones (LJ) liquid,[2] and the Broughton-Gilmer-Jackson model was thus proposed. This model depicts that the involved kinetic processes in the solidification of LJ liquid are mainly determined by the thermal motion of atoms. Furthermore, recent studies showed that an ultra-fast growth mechanism could be proposed for LJ systems and metals such as Al, Ni, Cu, Ag, Pt, or Pb.[3] These crystals can be grown without activated control. Therefore, ultra-fast growth kinetics can be employed. The models mentioned above all
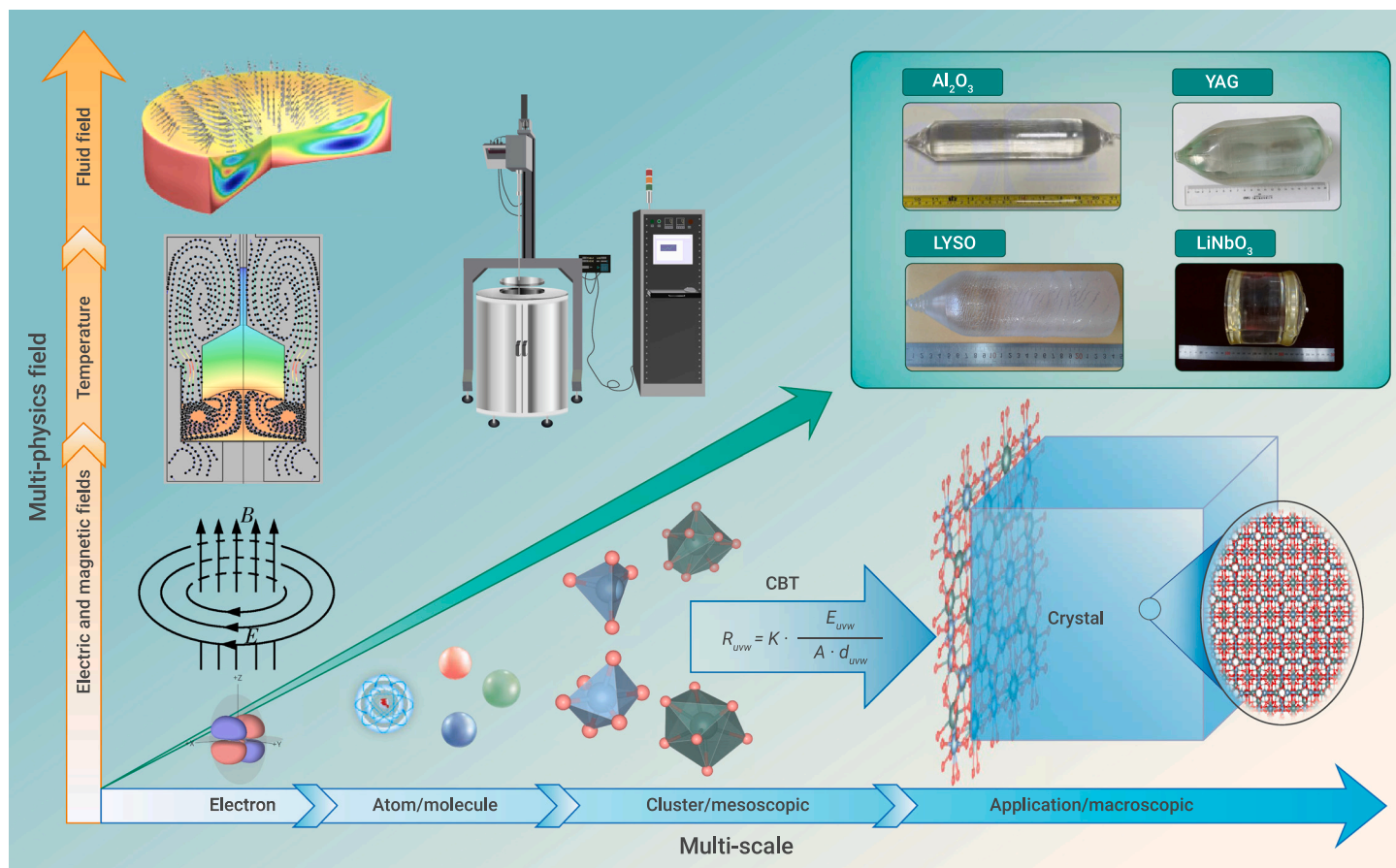

Figure 1. Schematic diagram of the multi-scale and multi-field coupling in a typical crystal growth system Clarifying growth mechanisms at both micro and meso scales is the key to decouple both multi-scale and multi-field thermodynamics/kinetics. Among them, chemical bonding theory (CBT) of single crystal growth can effectively predict both crystal morphology and growth rates. The horizontal axis represents crystal growth from electron to macroscopic scale. The vertical axis represents the existence of physics field in crystal growth system.

indicate that the crystal growth rate is related to system temperature. However, when overtaking a certain undercooling depth, Gao et al. show that the crystal growth rate in the solidification of colloidal particles may be independent of temperature,[4] in which the solidification of colloidal particles is a free-barrier process, and the crystal can grow rapidly under deep undercooled conditions.

Based on our research, the micro process of functional crystal growth is more complex. First, there are multiple structural units in the melts (or the liquids) after crystals melt; the type of these structural units has a critical impact on the phase transition path of the melts. Second, the proportion of various structural units would vary with the fluctuation of temperature, which may influence the kinetic process of crystal growth at different temperatures. Clarifying the mechanism of phase transition at the micro scale is the key to designing the crystal growth strategies. For example, our work showed that growing sapphire along the *c*-axis would be a complex process involving liquid-solid and solid-solid phase transitions. Therefore, it is necessary to design a suitable thermal field for stimulating the solid-solid phase transition at the interface, along with the liquid-solid phase transition at the solid-liquid interface.

At the mesoscopic scale, although many theories have been proposed, there are few simple and applicable theories. Based on the facts that minimizing free energy drives crystal growth, our team presented the chemical bonding theory (CBT) for the growth rate of crystal plane expressed by $R_{uvw} = K \cdot E_{uvw}/A \cdot d_{uvw}$, where K is a constant, E_{uvw} is the chemical bonding energy in the [uvw] direction, and d_{uvw} is the layer spacing.[5] Based on the CBT theory, the growth rate and crystal morphology of about 30 oxide crystals have been successfully predicted. Of course, there is still a gap between these mesoscale theories and the application of crystal growth.

At the macro scale, significant progress has been made by combining simulation and experiments. However, the preparation of large-size and high-quality crystals is still challenging, because the mechanisms on how different factors affect crystal growth are still unclear. Thus, it is difficult to rationally adjust these coupling factors at multiple scales. At present, only trial-and-error methods can be used to obtain the technology for a large-size single crystal, which is slow and costly commonly.

SOLUTIONS

A bottom-up approach that may be effective to solve this problem would include crucial aspects such as revealing the crystal growth mechanisms at the atomic and molecular scales, using finite element analysis methods to establish a multi-scale coupling model at both the micro and the macro scales, and implementing a full-scale simulation to elucidate the multi-factor/multi-scale issues in crystal growth. Of course, in this process, we are still facing the following difficulties.

Firstly, although the finite element simulation method at the macro level has been widely used to simulate crystal growth, multi-field coupling analysis of crystal growth by considering the electromagnetic, thermal, and fluid fields in the finite element analysis is still challenging. A great problem is the lack of parameters that can accurately describe the physical properties of the whole system, for example, viscosity, thermal conductivity, and density. Fortunately, artificial intelligence (AI) technology that has been widely used in modern materials research may bring new opportunities for multi-field simulation of crystal growth. Machine learning methods can be used to accurately obtain physical parameters or coarsening models of the melts and crystals under different conditions, which may provide a solution to the problem mentioned above. Leveraging the power of AI technologies, we may simulate the kinetic growth of crystals to reveal the roles of various factors in a specific system, making it possible to design a large thermal field matching the specific conditions for a system toward large-size crystals preparation.

Secondly, the region of solid-liquid interfaces should be better predicated. The position and morphological evolution of the solid-liquid interface are critical for crystal quality. In finite element simulation methods, only the isothermal surface has been used to describe the interface position and morphology. In fact, the growth or melting of crystals can also affect the interface position and morphology, as well as the distribution of isothermal surfaces near the interface. Of course, new isothermal surfaces would also alter the growth and melting of crystals. This indicates that existing methods to calculate the interface position would be inappropriate; the effects of crystal growth or melting should be taken into consideration, which can greatly improve the accuracy of crystal growth simulation. Adopting the CBT theory into the simulation algorithm would be an effective solution to crystal growth simulations. In the end, any breakthrough made in these two aspects as mentioned above will make significant progress in the research of crystal growth in aspects including the design of growth equipment, improvement of crystal quality, and enlargement of crystal size.

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DECLARATION OF INTERESTS

The authors declare no competing interests.