Crystals

Growth, Morphology and Perfection

Ichiro Sunagawa

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SUNAGAWA
Tohoku University

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Foreword to the English translation

The English version of this book was prepared based on translation by the author of the Japanese version; however, a few modifications have been made to assist the reader. The photographs appearing as plates at the front of the Japanese edition have been moved to the appropriate pages in the text, and references and suggested reading were moved to follow each chapter.

In preparing the English version, several individuals have assisted the author. Professor Andrew Putnis arranged the publication of the English version, and Professor Alan L. Mackay read through the manuscript and gave useful suggestions from a scientific standpoint. Dr. Sally Thomas and Irene Pizzie very carefully checked the manuscript and improved the English. The author sincerely appreciates their contributions. The permissions granted by many authors to reproduce figures from their various books and journals is gratefully acknowledged.

Preface

Crystals are solid materials having regular atomic arrangements characterized by periodicity and anisotropy. These properties are universally present, irrespective of whether the crystal is inorganic or organic, in living systems or in the inanimate world. Crystals exhibit various external forms, as represented by the elaborately varied dendritic forms of snow crystals or the hexagonal prismatic forms of rock-crystal. This variety of shape has stimulated scientific curiosity since the seventeenth century, since when intensive efforts have been made to understand the reasons why and how crystals can take a variety of forms.

The forms that crystals take result from the way in which crystals grow. The mechanism of growth is recorded in various forms in each individual crystal, regardless of size. The same crystal species may show different crystal forms (for example, polyhedral, skeletal, and dendritic), depending on growth conditions. Spiral growth step patterns, which record the growth process at the nanometer scale, have been observed on crystal faces. In single crystals, fluctuations in growth rates during the growth process are recorded as variations in perfection and homogeneity, such as growth sectors, growth banding, and three-dimensional distribution of lattice defects such as dislocations. The texture and structure of minute polycrystalline aggregate also record the growth history. These fluctuations are observed not only in crystals formed by inorganic processes, but also in those formed in living organs like bones, teeth or shells, or in calculus formed in various organs through the excretion of unnecessary components. To understand the phenomena occurring in complicated and complex systems, in which the growth process is unobservable *in situ*, we must regard the characteristics exhibited by crystal forms (morphology of crystals) as very important sources of information.

Our understanding of the atomic process and the mechanism of crystal growth progressed greatly during the latter half of the twentieth century. Various techniques have been developed that will produce bulk single crystals and thin films with high perfection and homogeneity by strict control of the growth parameters.

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Various crystalline materials with desired properties have been synthesized, and this has driven the utilization of single crystals in the production of semiconductor, opto-electronic, piezoelectric, and pyroelectric materials.

Understanding crystal growth mechanisms is just as important in the field of industrial crystallization, where a large quantity of minute crystals with well controlled sizes and forms are required, such as in pharmaceuticals, chemical seasonings or photographic emulsion, and even proteins. By coupling intellectual curiosity with the demands from industry, we have reached the point at which we can understand, at the atomic level, the mechanisms that determine crystal form, perfection, and homogeneity, at least in simple systems. It will be the task of researchers in the twenty-first century to deepen our understanding of phenomena that occur in more complicated and complex systems.

The main purpose of this book is to present the route that we need to take in order to decipher the phenomena and history occurring in complicated and complex systems, based on our present day understanding of simple and single systems. It is also hoped to present the root of the science and technology of crystal growth to those who are already actively involved in growing bulk single crystals and thin films using industrially established growth techniques.

The findings summarized in this book have been achieved through research activities by the author during half a century's work at the Geological Survey of Japan, Tohoku University, and the Yamanashi Institute of Gemmology and Jewellery Arts. Throughout this scientific career, a deeper understanding has been achieved thanks to my joint efforts with colleagues, and postgraduate and undergraduate students. I have unforgettable memories from individual research works, and, although no names are mentioned, I wish to express my sincere thanks to all those that have been involved. My thanks are also due to Ikuo Hirayama and Hideya Fukase of Kyoritsu Shuppan Co., for their overall support in publishing this book.

This book is dedicated to my wife, Michiko, and those unnamed others who have supported my research activities behind the scenes.

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PART I FUNDAMENTAL CONCEPTS

In Part I we summarize the fundamental concepts relating to the growth and morphology of crystals, such as atomic processes and mechanisms of crystal growth, and the principles governing the morphology, perfection, and homogeneity of crystals. We base this description on a historical review of the development of the subject. Such fundamental concepts relating to atomic processes and the mechanisms of crystal growth have been acquired throughout the twentieth century through investigations on simple systems and the single phase, and have formed a base for the development of industries, such as semiconductors, in which single crystals are used. Our understanding of the phenomena occurring in complicated and complex systems, such as in the formation of solid earth materials or biomineralization, will be deepened based on the fundamental concepts explained in Part I.

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1

Introduction

The crystal, with its regular atomic construction, is the most commonly encountered state of solid materials. The three properties of a crystal, external form, perfection, and homogeneity, are directly related to how the crystal grows. Individual crystals of the same species and atomic construction may have different properties. The mechanism of crystal growth has long been understood at an atomic level, at least for simple systems. Our understanding of the factors determining external form, perfection, and homogeneity provides us with the information necessary for the development of industries which utilize the physical properties of single crystals in forms of bulk and thin film, such as semiconductors. In the twenty-first century, we expect to clarify the relevant phenomena occurring in complex and complicated systems.

1.1 Historical review

On hearing the word "crystal," most of us call up images of regular, symmetric forms, perhaps the prismatic form of rock-crystal, or the dendritic form of snow crystals. We use the term "crystal clear" to imply something transparent and pure. The ancient Greeks used the term crystal (κρνσταλλο) to imply clear, transparent, and hard ice; rock-crystal was so named as it was thought to be unmeltable ice that existed in fissures of rocks. As in the present day, the regular polyhedral forms were the ones that roused the most interest. Pythagoras, for example, used the word crystal to imply perfection, harmony, and beauty; and Plato listed his famous five polyhedra, related to fire, earth, air, water, and the universe.

Theophrastos (372–287 BC), the author of the oldest book on minerals, *On Stones*, referred briefly to regular polyhedral forms exhibited by mineral crystals [1]. In later books on minerals, polyhedral forms bounded by mirror-flat faces are mentioned.

For example, in the lengthy *Natural History* [2], by the famous Roman natural historian Gaius Plinius Secundus, there are descriptions of polyhedral forms of beryl, rock-crystal, diamond, etc.

It was not until the seventeenth century, however, that special attention was paid to the *forms* of crystals. Kepler was deeply attracted by the highly varied dendritic forms of snow crystals, and he believed that the units constituting snow crystals were equally sized spheres [3]. Kepler described the observed elaborately varied external forms as simply the result of the combination of these spherical units. This marked the beginning of the concept of crystal structure. Starting from Kepler's idea of equally sized spheres as the constituent units, the concept was developed to include equally sized ellipsoidal units by Huygens, and further to polyhedral units by Haüy. These were systematized into seven crystal systems based on the axial lengths and axial angles, and were further subdivided into thirty-two crystal groups (point groups) by the combination of symmetry elements compatible with the seven crystal systems. In the Appendixes we present: the crystal axes; the fourteen Bravais lattices and the seven crystal systems; the indexing of crystal faces and zones; the symmetry elements and their respective symbols; and the stereographic projections of the thirty-two crystal groups. These are mathematical systems, but numerous observations on the real crystals of minerals formed the basis for this ordering. Based on this mathematical structure, the forms exhibited by polyhedral crystals were investigated, and the relationships between these forms and the lattice types were discussed. This type of investigation is called crystal morphology, and was of great interest in the nineteenth and early twentieth centuries. A vast amount of data of descriptive and classification type were accumulated during this period. The results were complied in books such as Goldschmidt's *Atlas der Kristalformen* and Dana's *The System of Mineralogy* (see refs. [1] and [4], Chapter 9).

In 1912, Von Laue demonstrated using X-rays that a crystal is constructed of unit cells, and that it is possible to determine atomic positions by means of diffraction phenomena. Investigations analyzing crystal structure spread quickly, and within a short period the crystal structures of most simple inorganic crystals had been analyzed, deepening the knowledge of chemical bonding and atomic and ionic radius, and leading to the emergence and rapid progress of a new scientific discipline, crystal chemistry. It was during this period that the importance of the 230 space groups, which had been mathematically introduced by Federov, Schoenflies, and Barlow, was pointed out by a Japanese researcher, S. Nishikawa, in analyzing crystal structures. In addition to X-rays, electron and neutron beams are now also used in structural analyses; nowadays, stronger X-ray beams are used, and there have been great developments in the apparatus used for structural analyses, which have now become almost routine, except for crystals of macromolecular proteins.

1.2 The birth of the concept of crystal growth

In the seventeeth century, the Danish anatomist Nicolaus Steno (1638–1687) collected many samples of rock-crystals, and he measured the interfacial angles of hexagonal prisms. He found that the interfacial angles of corresponding faces were constant, irrespective of external form. This was the beginning of the now accepted "law of the constancy of interfacial angles." In the treatise describing his finding, Steno put forward two important concepts. He argued that rock-crystals were not of organic origin formed by the activity of bacteria in the soil, as was widely believed, but that they grew through the agglutination of tiny particles formed through inorganic processes taking place in high-temperature aqueous solution. He explained that the reason why rock-crystals show hexagonal prismatic forms bounded by six triangular faces at the tip and six rectangular faces, and sometimes show tapering prismatic or platy forms, is that the growth rates are different depending on crystallographic direction, i.e. on the different crystal faces [4]. These concepts of crystal growth and growth rate anisotropy provide a basis for the present-day science of crystal growth.

Interest in crystal form continued into the eighteenth century. Hooke noted that alum crystals took regular octahedral forms when they grew on the tip of a string immersed in aqueous solution, whereas their forms changed into platy triangular or hexagonal platy, though bounded by the same faces, when they grew at the bottom of a beaker (see ref. [11], Chapter 4). De l'Isle reported that when NaCl crystals grew in aqueous solution containing a small amount of urea, they took a simple octahedral form, in contrast to the simple cubic form grown in pure solution (see ref. [26], Chapter 4).

In the nineteenth century, when crystal morphology was systematized to fourteen types of unit cells, seven crystal systems and thirty-two crystal groups, the following two macroscopic treatments on the morphology of crystals emerged.

(1) The Bravais empirical rule, which states that there is a close correlation between the polyhedral forms of a crystal and the lattice type.
(2) Theoretical treatments by Gibbs, Curie, and Wulff on equilibrium form showed that the equilibrium form of a crystal having anisotropy should be polyhedral, not spherical, as would be expected for the equilibrium form of an isotropic liquid droplet. (See refs. [6]–[8], Chapter 4.)

It became necessary to understand how crystals grow at the atomic level so as to form a deeper understanding of why crystals can take a variety of forms. This was achieved through the layer growth theory put forward in the 1930s by Volmer, Kossel, and Stranski on the structure and implication of the solid–liquid interface, the spiral growth theory by Frank in 1949, and the theory of morphological

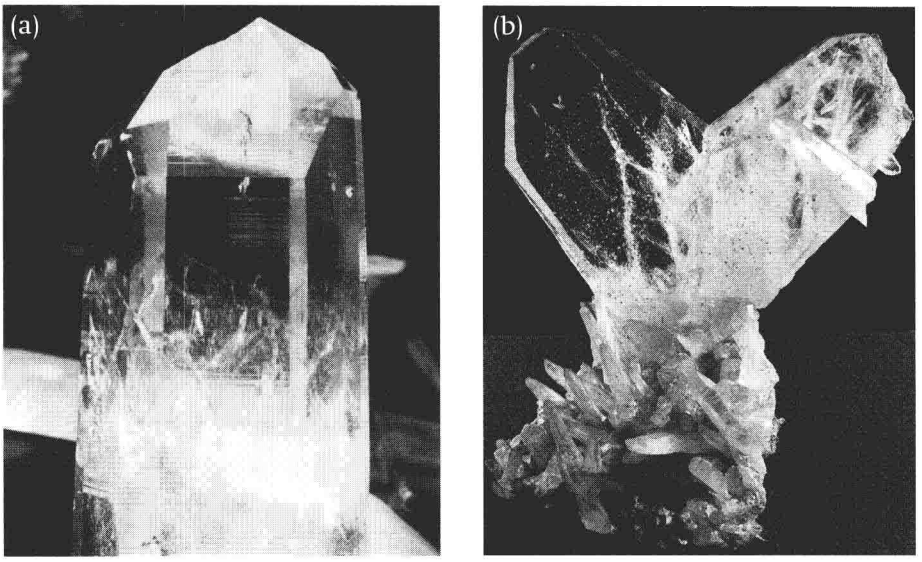

Figure 1.1. (a) This hexagonal prismatic form of rock-crystal appears due to spiral growth on smooth interfaces and growth rate anisotropy. (b) Twinned rock-crystals from the Otome Mine in Japan. According to the Japan Law (see Section 10.6), these are larger and show a more flattened form than the coexisting single crystals.

instability by Mullins and Sekerka in 1963 (see refs. [7]–[11] and [20], Chapter 3). The understanding of the mechanism of crystal growth progressed experimentally in the twentieth century. Before the 1930s, the main work was performed on the relationship between the macroscopic ambient phase and macroscopic crystal forms. Later, advancements in optical microscopy and electron microscopy made it possible to observe and measure growth spirals with step heights of nanometer order. It is now possible to observe the behavior of spiral step advancement of nanometer order in height *in situ*.

1.3 Morphology, perfection, and homogeneity

Since the growth mechanisms of crystals have become understood at the atomic level, at least in single and simple systems, it has become clear how the micromorphology (the morphology of growth spirals and etch pits) and the macromorphology (polyhedral, skeletal, and dendritic forms) of crystals are determined. Since the morphology of crystals is the result of crystal growth, this is related to how lattice defects (point, linear, and planar) are induced and distributed in single crystals, and to how impurity elements participate. This leads to the development of the method of controlling perfection and homogeneity of bulk and thin film

single crystals and to the exploration of semiconductor and opto-electronic materials with desirable properties. It is with these developments that today's industries are concerned.

1.4 Complicated and complex systems

Knowledge of the growth mechanism, morphology, perfection, and homogeneity of single crystals creates a base from which we may understand the morphology exhibited by polycrystalline aggregates, or the mechanism of formation of textures and structures that appear in polycrystalline aggregates of multiple phases, such as those shown by ceramics, metals, and rocks.

Many examples are known to exist that show that polycrystalline aggregates exhibit properties different from those of single crystals. For example, on the Mohs scale the hardness of diamond is given as 10, the highest for any known mineral, yet a diamond single crystal is weak to shock due to the cleavage. It is due to the textures formed by polycrystalline aggregation that carbonado and ballas, polycrystalline aggregates of diamonds, have higher toughness and can be used as boring heads, unlike the relatively weak single crystals. Similarly, the toughness of bamboo results from the textures formed by aggregation of soft cells. The outer and inner skins have different textures and different functions.

What determines the physical forms of animals and plants is a subject of much debate within the biological sciences. We know that the basic unit of living bodies is not crystalline; however, should we entirely disregard the units that comprise living organisms as having no link to crystals? Does DNA alone uniquely control all living phenomena?

There are inorganic and organic crystals formed in living bodies as a result of being alive, and these are the link between living phenomena and crystals.

Tooth, bone, shell, and the exoskeleton are formed to maintain life, whereas gallstones, bladder stones, and sodium uric acid (a cause of gout) are the results of excretion processes of excess components. Tooth, bone, and shell are composed of inorganic crystals of apatite, aragonite, calcite, and protein. It is assumed that these crystals grow through the cooperation of both crystals and proteins. Teeth consist of enamel and dentine portions, both constituting aggregates of apatite crystals of different forms and sizes, leading to different textures and functions. In contrast to well controlled forms, sizes, and textures of these polycrystalline aggregates formed by cooperation with protein, crystals constituting calculi in organs, such as gallstones, usually exhibit uncontrolled radial polycrystalline aggregations, suggesting no cooperation between protein and crystals.

It is conjectured that there can be two types of cooperation with proteins for

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