

GROWTH OF AMMONIUM HALIDES, CADMIUM
OXIDE AND ZINC OXIDE CRYSTALS FROM
VAPOR PHASE AND SOLUTION TECHNIQUES

By

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P R E F A C E

Crystals have been admired by man for as long as he has appreciated beauty. For the scientific and technological society, the basis of the beauty is the perfection and purity of these crystals. Earlier, most of the scientific studies were conducted almost exclusively on powdered samples in doped and undoped states. Although these investigations did set forth a basis for understanding of various properties of materials, much of our present knowledge has been gained through studies on single crystals. Besides, single crystals are preferred over polycrystalline samples for the reproducibility of results and for the fabrication of devices.

The essential requirement of the materials in the form^m of single crystals of higher purity and perfection has led to extensive work in the field of crystal growth. The crystals required for various studies often vary in size ranging from platelets and whiskers to large single crystals. It is therefore important both from scientific and technological points of view to understand and establish the growth conditions for different morphologies. There is always a need to search for new and easy methods for growing ~~any~~ single crystals to overcome various technological

difficulties. The knowledge and experience of a large number of growth techniques enables one to devise new methods for the growth of single crystals of particular materials. The basic techniques are growth from solution, vapor and melt; other techniques are either combinations or modifications of these techniques. In the work reported in this thesis solution and vapor phase techniques have been used to grow single crystals of NH_4Cl , NH_4Br , CaO and ZnO .

NH_4Cl and NH_4Br were chosen for growth because of the recent wide spread interest in the understanding of order-disorder phenomenon. Both NH_4Cl & NH_4Br undergo λ type order-disorder transitions at 242.8°K and 235°K , respectively⁽¹⁾. The ordered phase of NH_4Cl is analogous to Ferromagnetism while ordered phase of NH_4Br is analogous to antiferromagnetism. Above T_λ both have disordered phase with tetragonal structure, i.e. NH_4 tetrahedra are randomly distributed between the two inverted configurations and below T_λ complete order is attained. In NH_4Cl , NH_4 tetrahedra are similarly oriented while in NH_4Br they exist in pair of inverted molecules of unit cell. NH_4Cl and NH_4Br single crystals are also of interest for the understanding of transport mechanism as

¹ C.H.Wang and P.A. Fleury in "Light Scattering in Solids"
Ed. G.E.Wright (Springer-N.Y.1969) p. 651.

they exhibit all the three modes - electronic, ionic and protonic -- of conduction. All these properties are very sensitive to the purity and perfection of crystals. The crystals studied earlier were grown from solution in the presence of impurities which are essential to grow polyhedral crystals of ammonium halides.

Very recently Ebisuzaki^(2,3) have made n.m.r. study and electrical measurements on crystals grown from solution in presence of urea and those from vapor and have found that these properties differ considerably, showing that the solution grown crystals are relatively less pure and less perfect than vapor grown crystals. As no report was earlier available on the detailed study of growth of high purity ammonium halide crystals, a detailed investigation to find a suitable technique for the growth of these crystals of various morphologies and of high purity was taken-up. Vapor phase technique was, however, found to be successful and has been used for growth and to study the growth kinetics of these crystals.

With the increasing interest in the investigation^{of} "disordered structures", the interest grows also in

² Y. Ebisuzaki, J.Chem.Phys. 61(8), 3170 (1974).

³ Y. Ebisuzaki, J.Crystal Growth 26, 301 (1974).

the studies of electrical and optical properties of a highly degenerate semiconductor. Because single crystal preparation is extremely difficult, physical measurements in past have been made mostly with sintered materials or with specimens prepared by cathod sputtering. Only a few reports are available on the growth of single crystals of CdO, and they employ high growth temperatures which result in high vacancy concentration of oxygen and hence high electrical conductivity with very mild temperature dependence⁽⁴⁾. However, in a low temperature range $\leq 400^{\circ}\text{C}$ the variation of electrical conductivity of samples made of CdO powder with temperature was found to be very pronounced. Therefore attempts were made to grow single crystals of CdO at lower temperatures than those employed by other workers trying the methods used for the growth of other oxide materials. Two out of many attempts made have been successful and are described in the thesis.

ZnO has been chosen for the growth as no simple and suitable method is known for the growth of its single crystals⁽⁵⁾; earlier used methods of growth invariably employ high temperatures. This material is known to be

⁴ F.P. Koffyberg, J. Solid State Chem. 2, 176 (1970).

⁵ S.C. Kashyap, Ph.D. Thesis, IIT Delhi (1972)

of tremendous technological importance as it is being used for the fabrication of a large number of solid state devices. Also, there is always a need to understand the mechanism of growth and to develop easy growth methods.

The work reported in the thesis has been mainly divided into two parts: the first part deals with the growth of ammonium halides and the second part with ZnO and CdO crystals of various morphologies. Part I has been sub-divided into three chapters. Chapter I describes the study of the Piper and Polich technique for the growth of large size single crystals of ammonium chloride, the effect of phase transformation on the crystalline nature of the material and the growth of needle shaped crystals and small polyhedral crystals using open tube sublimation technique. Thermal etching of these crystals has also been made. Various mechanisms involved in the evaporation and growth of the crystals have been discussed.

Chapter II deals with the growth of three dimensional highly symmetrical dendritic crystals of ammonium chloride. A brief account of the various existing theories of dendritic growth have been given and the morphological features of the grown crystals are discussed on the basis of these theories. The growth kinetics and the effect of thermal diffusion, water vapor, vacuum and the presence of HCl gas on the growth and morphology of the crystals are discussed.

Chapter III deals with the growth of crystals of various morphologies of ammonium bromide employing open tube sublimation technique. A comparison of these crystals with those of ammonium chloride described in Chapter II has been made. The differential behaviour of the two materials has been discussed.

Part II of the thesis has again been sub-divided into three chapters. The first chapter of this part (Chapter IV) deals with the growth of whiskers, needles and platelet crystals of CdO by vapor phase technique in which cadmium vapor produced by thermal decomposition of cadmium oxalate were oxidized by the atmospheric oxygen at 650°C. Conditions of growth and the possible mechanism involved have been discussed.

Chapter V discusses the growth of cadmium oxide crystals of rhombododecahedron morphology of size $15 \times 1.5 \times 1.5 \text{ mm}^3$ using flux technique. The crystals grow at comparatively lower temperature than in the earlier used methods for the growth of CdO crystals. It has been observed that unlike other flux growth experiments, supersaturation in the present case is caused by the dissociation of some complexes unstable at high temperature. The effect of growth temperature and of cooling rate on the morphology of the crystals has also been discussed.

The last chapter (Chapter VI) describes the growth of needle-shaped hollow crystals of ZnO using flux technique. The molten hydrous KOH was used as solvent. The effect of growth temperature on the morphology of crystals has been studied. The growth of hollow crystals has been attributed to the impurity modified hopper growth and to impurity adsorption.

A part of the work has resulted in the following research publications:

1. On the growth of single crystals of ammonium chloride from vapor phase techniques.
S.D.Sharma and Krishna Kumar
J. Appl. Phys. 45(9), 4120 (1974)
2. Growth of ammonium chloride dendrites from vapor phase
S.D.Sharma and Krishna Kumar
Jap. J. Appl. Phys. 13(11), 1109 (1974).
3. On the growth of ammonium bromide crystals of various morphologies.
Krishna Kumar
Ind. J. Pure and Appl. Phys. 12(7), 519 (1974).
4. Growth of ammonium chloride dendrites from vapor phase

S.D.Sharma and Krishna Kumar

Presented at the Indo-German Conference held at
IIT Madras on February 26, 1974.

5. Growth of Hollow Crystals of ZnO by flux method.
Krishna Kumar
J. Crystal Growth 26, 200 (1974).
6. Growth of Single Crystals of CdO from molten
hydrous KOH solution.
Krishna Kumar
J. Electrochemical Soc. 122(8), 1142 (1975).
7. Growth of needles and whiskers crystals of CdO
by thermal decomposition of cadmium oxalate.
Krishna Kumar
(Communicated for publication).
8. Habit modification and NH_4Cl in presence of
urea and pectin.
Krishna Kumar (to be communicated)
9. A Study of the inhomogenities in microglass
slides.
Krishna Kumar (to be communicated).

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