

**GROWTH AND STRUCTURE OF PURE AND
MIXED CADMIUM-HALIDE CRYSTALS**

by

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Submitted

**in fulfilment of the requirements of the
degree of Doctor of Philosophy**

to the

Indian Institute of Technology, Delhi.

November, 1976.

ACKNOWLEDGEMENTS

I am highly indebted to Dr. S.D. Sharma for the valuable guidance rendered by him throughout my work. His constructive suggestions and encouragement in my work have been of immense help to me. In fact, it has imparted me considerable inspiration and enthusiasm for overcoming the various problems encountered during my research work.

I am thankful to Dr. V.K. Agarwal for his helpful suggestions and keen interest throughout my work. His contribution has proved to be of great help to me.

I am grateful to Prof. A.K. Ghatak, Prof. C.L. Mehta and Prof. K.L. Chopra, for extending all research facilities, required for my work.

I am thankful to Dr. L.K. Malhotra, Dr. S.C. Kashyap and Dr. S.K. Sharma for their continued interest in my work. I highly appreciate the cooperation extended by my all colleagues and friends, particularly "Miss Neeta Bhargava," during my work.

Thanks are due to Director, Indian Institute of Technology, New Delhi and the Council of Scientific and Industrial Research, New Delhi, for the award of research fellowships. I also offer my thanks to Mr. N.S. Gupta for preparing the drawings and to Mr. Ranjit Kumar for the typing of the thesis.

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PREFACE

Many inorganic compounds and minerals are known to crystallize in a large number of crystallographic modifications called polytypes. Polytypism was discovered in 1912 but to-date no single theory explains all the observed facts. Few scattered reports have appeared in the literature from time to time suggesting growth conditions or impurities as a plausible cause of polytypism. But the only theories which have received good experimental recognition so far, are the Frank's dislocation theory and Jagodzinski's disorder theory. But these theories too, do not explain all experimental results.

For the understanding of the phenomenon in its entirety it seemed necessary to have an idea whether polytypism is a consequence of the spiral growth mechanism or it has a definite thermodynamic basis. Thus CdI_2 and CdBr_2 , well known polytypic substances, were chosen for the present investigation. A large number of reports on growth and polytypism in CdI_2 and CdBr_2 crystals have appeared in the literature; however, except for a couple of attempts, these crystals have been grown from solution employing isothermal evaporation technique under rather undefined conditions.

In the present investigation, crystals were grown

under stabilized conditions; the growth mechanism and structure were studied in detail. Impurities were deliberately added in the crystals to investigate the effect of impurity. High resolution optical microscopg, scanning electron microscopg, transmission electron microscopg and x-rays were used as tools for the study.

The work reported in the thesis has been divided into five Chapters. Chapter I reviews the theories of growth and polytypism.

Chapter 2 describes the growth of CdI_2 and CdBr_2 dendrites and platelets by the vapour phase technique. Vapour phase method was selected because it gives better control over growth variables and facilitates growing high perfection crystals. The growth mechanism was studied in details using high resolution optical microscope and scanning electron microscope. No spirals were observed on the crystals which grow with their basal planes normal to the wall of the growth tube, whereas spirals have been observed on crystals grown at glass substrate at comparatively higher supersaturation. The observations indicate that the growth does not take place by the screw dislocation mechanism. The growth starts with the dendritic skelton and then changes to flat platelets by the filling in process, and two dimensional nucleation. Formation of spirals on crystals grown on glass slides has been attributed

to adsorbed impurities or debris and irregularities on the substrate surface.

Chapter 3 deals with the transmission electron microscopic studies of the as-grown crystals. The crystals possess good perfection and show dislocation networks and loops. The stacking faults are not common in the crystals. The decomposition of the crystals under electron microscope has been also studied in detail. Due to decomposition cadmium metal is crystallized and halogen gas is liberated. A number of micrographs and electron diffraction patterns have been taken at different stages of decomposition. Double diffraction patterns in CdI_2 as well as in CdBr_2 confirm the decomposition mechanism.

X-ray investigation of vapour grown CdI_2 and CdBr_2 crystals are detailed in Chapter 4. Nearly all vapour grown crystals show the most stable basic polytype of the substance (4H in CdI_2 and 6R in CdBr_2). Screw dislocation and Jagodzinski theories are discussed in the light of present observations. Observations indicate that conditions of growth play an important role in deciding the structure.

The last Chapter of the thesis includes the growth and structural analysis of mixed crystals. Impurities were added in the CdI_2 crystals and the growth mechanism

(iv)

was studied. The $\text{CdI}_{2-x}\text{Br}_x$ and $\text{CdI}_{2-x}\text{Cl}_x$ crystals mainly show 4H and 12R (obverse and/or reverse) polytypes and also 2⁴R in a few cases. As other conditions of growth were similar to those for the pure crystals, the change observed in the structure has been attributed to impurities present in the system. Thus the presence of impurities can lead to the formation of new polytypes.

The present growth and structural analysis observations have thrown further light for a better understanding of the phenomenon of polytypism. The author has concluded from the observations presented in this thesis that growth conditions and the presence of impurities are very important in determining the structure of polytypic substances.

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CONTENTS

	<u>Page</u>
PREFACE	(1)
CHAPTER 1 INTRODUCTION	1
1.1 Growth From Vapour Phase Technique	1
1.2 Theories of Crystal Growth	2
1.3 Polytypism	12
1.4 Theories of Polytypism	12
CHAPTER 2 GROWTH OF CADMIUM HALIDE DENDRITES AND PLATELETS BY VAPOUR PHASE	36
2.1 Experimental	38
2.2 Observations	40
2.3 Discussion	57
Summary	71
CHAPTER 3 ELECTRON MICROSCOPIC STUDY OF DEFECTS AND DECOMPOSITION OF CADMIUM HALIDE CRYSTALS	72
3.1 Structure of Cadmium Halide Crystals	74
3.2 Defects in Cadmium Halide Crystals	75
3.3 Decomposition of the Crystals	78
Summary	101
CHAPTER 4 POLYTYPISM IN PURE CADMIUM HALIDE CRYSTALS	102
4.1 Structure of Cadmium Iodide and Cadmium Bromide	105
4.2 Direct and Reciprocal Lattice of CdI ₂ and CdBr ₂ Structures	108
4.3 c-dimension of Polytypes	112
4.4 X-ray Diffraction Photographs	113
4.5 Results	115
4.6 Discussion	118
Summary	125

	<u>Page</u>
CHAPTER 5 GROWTH AND POLYTYPISM IN MIXED CADMIUM HALIDE CRYSTALS	126
5.1 Experimental	128
5.2 Growth Observations and Mechanism	130
5.3 X-ray Results	137
5.4 Structures of Crystals	144
5.5 Discussion	145
Summary	148
BIBLIOGRAPHY	149
ABOUT THE AUTHOR	159
LIST OF PUBLICATIONS	160