

POLYTYPISM AND GROWTH IN CADMIUM HALIDE CRYSTALS

by

Ganpat Lal Sharma

Thesis submitted to the Indian Institute of Technology, Delhi
for the award of the Degree of
DOCTOR OF PHILOSOPHY

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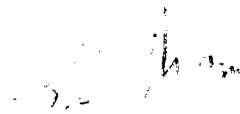
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(Ganpat Lal Sharma)

PREFACE

In the past three decades, a number of reports have appeared in the literature on polytypism, a phenomenon which arises from the capacity of certain close packed and layered solids to crystallise into more than one modifications. Still, further effort is required before it can be explained or understood fully. In the present work polytypism and growth kinetics have been studied in crystals of cadmium halides by employing x-ray diffraction and electron microscopic techniques. High resolution optical microscope and scanning electron microscope (SEM) were used to study the surface features of the crystals and to understand the possible growth mechanism at different stages of growth. To find the perfection and disorder of the crystals, transmission electron microscopic (TEM) studies were performed. The pure and mixed crystals of cadmium halides were chosen for investigation mainly because in cadmium bromide and $\text{CdBr}_{2-x}\text{I}_x$ crystals the phenomenon is practically not studied and also the growth conditions leading to various polytypes are not well established.

The work reported in the thesis has been divided into six chapters. Chapter I deals with a brief review of the phenomenon of polytypism, its occurrence and theories put forward to explain it alongwith the growth techniques with a special reference to cadmium iodide and bromide.

Chapter II deals with the microscopic, x-ray and electron diffraction techniques for understanding the growth

processes involved in the vapour grown CdI_2 crystals. 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, on glass substrate, at comparatively higher supersaturation. In the early stages of layer growth, or whenever a fresh nucleation takes place, the most probable structure is observed to be a non-periodic one dimensionally disordered structure. The disordered structure, as growth proceeds, changes into an ordered one.

Chapter III describes the direct and reciprocal lattices of cadmium halides and different experimental procedures to obtain x-ray oscillographs. X-ray diffraction is very suitable for the study of polytypism in cadmium halides. The procedure for taking x-ray oscillographs and their interpretation has been discussed in detail. X-ray diffraction studies made on crystals grown under conditions of imposed thermal fluctuations showed 4H alongwith 12R polytype. A large number of solution grown CdBr_2 crystals upon x-ray examination exhibited the unusual phenomenon of rotation during their growth; the angle of rotation is $\sim 4^\circ$ between the two opposite basal faces of the crystal.

Chapter IV discusses the procedure adopted for finding the structure of cadmium halide polytypes. Structural determination of polytypes is an important aspect of the study of polytypism. However, for polytypes with longer periodicities, the problem of structure determination is not so simple. The detailed procedure for structure determination of polytypes has been outlined. A fortran programme for the calculation of relative intensities of different 10.1 spots has been worked out. The complete crystal structure of a new rhombohedral polytype 12R of cadmium bromide has been determined. Its formation has been explained by layer transformation mechanism.

Chapter V gives an account of the electron microscopic studies of the as grown crystals. During prolonged studies the crystals got decomposed and their decomposition has also been studied in detail. Due to decomposition cadmium metal is crystallised 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 CdBr_2 confirm the decomposition mechanism.

The last chapter of the thesis includes the growth and structural analysis of mixed crystals. The formation of mixed crystals has been confirmed by employing various techniques.

The relative amount of the different elements present in the as grown crystals were determined by using scanning Auger microscopy.

The author has concluded that growth conditions and the presence of impurities are very important in the formation of various polytypic structures of a compound. The work presented in the thesis has thrown further light for a better understanding of the phenomenon of polytypism and has resulted in the following publications/communications.

1. "Comparative Study of Pure and Mixed Cadmium Halide Crystals", presented at the Tenth National Conference on Crystallography, Varanasi, p. 73, 21-23 Feb. 1979.
2. "Dependence of Polytypism on Growth Conditions in Cadmium Iodide", presented at the 11th National Conference on Crystallography, Calcutta, G-6, 17-19 Jan. 1980.
3. "Effect of Growth Conditions on Polytypism in Cadmium Iodide" (communicated).
4. "The Crystal Structure of a New Polytype 12A of Cadmium Bromide", Acta Cryst. B36 (1980), 26.
5. "Growth Mechanism of Cadmium Iodide Polytypes", J. Crystal Growth 49 (1980), 580.

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