Proc. Indian natn. Sci. Acad., **57**, A, No. 2, 1991, pp. 231-239.
© Printed in India

VAPOUR GROWTH AND CHARACTERIZATION OF CADMIUM IODIDE DENDRITIC SINGLE CRYSTALS

BINAY KUMAR AND G C TRIGUNAYAT

Department of Physics and Astrophysics, University of Delhi, Delhi-110007, India

(*Received* 22 *December* 1989; *Accepted* 30 *November* 1990)

Both analar grade and highly purified cadmium iodide have been used to grow dendritic single crystals from vapour. Surface growth features and polytypic behaviour of these dendrites have been studied and interpreted. X-ray diffraction methods have been employed to characterize the dendrites for their polytypism and related behaviour. The surface growth features have been studied by optical and scanning electron microscopy. The X-ray diffraction photographs have shown exclusive presence (100%) of the most common polytype 4H in the case of pure CdI_2 dendrites. In the microscopic surface studies, usual dendritic growth features have been observed.

Key Words : Dendritic Growth; Cadmium Iodide; Polytypism; Structural and Morphological Characterization

Introduction

Dendrites possess a tree-like growth form, having a stem and branches of different orders, extending in unique crystallographic directions. Dendritic growth has been frequently observed for several metals, grown by various techniques like melt[1], liquid solution[2] and vapour[3]. So far, all experimental studies of the phenomenon of polytypism have been carried out on crystals grown in a form other than dendrites e.g., plates, needles, prisms, etc., although crystals of a very wide variety have been grown and several different techniques have been employed for growing them, e.g., solution growth, melt growth, gel growth, etc[4]. In the present work, it was proposed to grow dendritic single crystals of cadmium iodide from vapour phase under controlled conditions and study their polytypism. Cadmium iodide was chosen because it is known to be a strongly polytypic material. Nearly 193 polytypes of CdI_2 with known crystal structures have been discovered so far[5]. The work plan consisted of four parts:

(*a*) purification of cadmium iodide by zone refining;
(*b*) growth of dendritic single crystals of cadmium iodide from vapour;
(*c*) x-ray diffraction study of polytypism and related phenomena; and
(*d*) study of surface growth features by optical and scanning electron microscopy.

The results have been discussed in the light of current knowledge of the phenomenon of polytypism.

Experimental

Purification of Material

Both analar grade cadmium iodide, supplied by M/s Fluka, Switzerland, and highly purified cadmium iodide, were employed for crystal growth. The purifica-

tion was carried out by zone refining. The apparatus used for this purpose was similar to that used earlier by Chaudhary and Trigunayat[6]. Some modifications were incorporated in the shapes of heater and boat and in the system for zone movement, which led to (*i*) smaller melt zone width (less than 1cm) and (*ii*) flat solid melt interface. As many as twenty zone passes were given to obtain almost impurity-free material. The highly pure material residing in the middle portion of the ingot was used for subsequent crystal growth from vapour phase.

Crystal Growth

The furnace used for crystal growth is shown in Fig. 1. Its temperature profile is depicted in Fig. 2. The crystals were grown both in argon atmosphere and in vacuum. A glass tube of diameter 3cm and length 1m, with one end tapered, was employed for crystal growth in argon atmosphere (purity of argon = 99.99%). The tube was placed symmetrically in the furnace and the gas was blown through the tapered end for half-an-hour, after which both the ends of the tube were closed. Then the temperature was gradually raised to 520°C. Powdered cadmium iodide was taken in a small glass up (water capacity 1ml), which was inserted in the tube and placed at the centre of the furnace. Within 8 to 10 hours, dendrites were seen to have formed nearly 10cm away from the centre (i.e., the charge). They were found hanging perpendicular to the tube axis, with one end stuck to the wall of the tube. Subsequently, the temperature of the furnace was gradually lowered, beginning with a slow rate. The tube was removed and the dendrites were carefully collected on a soft tissue paper.

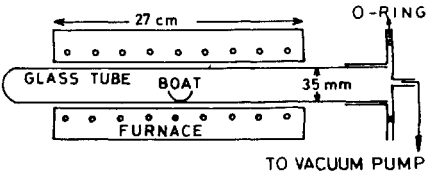

Fig 1 Experimental set-up for growing dendritic single crystals of cadmium iodide

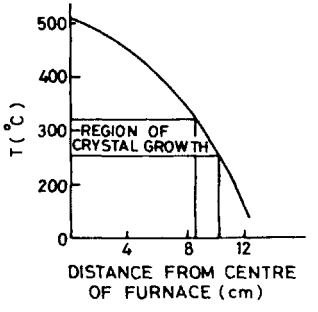

Fig 2 Temperature profile of the furnace employed for crystal growth

For crystal growth in vacuum, another glass tube having one end closed was employed. The open end was rendered air-tight by fitting it with a metallic flange[7]. A rotary pump was connected with the tube through the flange to evacuate the tube. The charge was placed inside the tube and the tube was evacuated for about half an hour. A vacuum of the order of 10^{-2}-10^{-3} torr was obtained. Then the tube was placed in the furnace and crystal growth was carried out as before.

Structural Investigations

For the X-ray diffraction study, a dendrite was stuck to a glass fibre and suitably mounted on the goniometer head of the X-ray camera. Oscillation photographs were taken in the oscillation range 25-40° (i.e., angle made by the *c*-axis of the dendrite with the incident X-ray beam varied between 25° and 40°). This range enables to record a large succession of 10.1 reflections, which are particularly helpful in a quick identification of polytypes. Nearly 25 dendritic single crystals were examined. Because of the large size of the dendrites (average size 7×3 mm^2) and in view of the fact that CdI_2 crystals are known to exhibit parallel growth of two or more polytypes on the same face of a crystal, oscillation photographs were taken from 4-5 different portions of a dendrite face. The portions of particular interests on a face were tip, stem, primary arms, secondary arms etc. Altogether 142 oscillation photographs were taken and studied. All photographs were recorded on a cylindrical camera of radius 3cm, employing Ni-filtered CuK_α radiation.

Study of Surface Growth Features

The surface growth features were studied by optical microscopy and scanning electron microscopy. For optical microscopy, a given dendrite was so mounted in front of the microscope objective that its basal plane lay parallel to the principal focal plane of the objective. In all, nearly 50 photographs were taken, employing objectives of focal lengths ranging from 4mm to 33mm, both in transmission and in reflection modes. Greater emphasis was placed on those portions of the dendrites that had revealed information of special interest on their X-ray diffraction photographs.

For SEM studies, a JEOL scanning elecron microscope model HSM 840 was employed. A dendrite was stuck on a brass block by means of silver plate. Subsequently, a heavy fine sputtering of gold on the crystal became necessary, as cadmium iodide is an insulator.

Results and Discussion

The as-grown dendritic crystals approximately measured between 3×2mm^2 and 10×6mm^2. Their thickness varied between 0.1mm and 0.6mm. The photograph of a dendrite is shown in Fig. 3. Most of them had well separated primary and secondary arms. On the other hand, a few crystals had spaces between the arms completely filled. Most of the crystals looked shining and transparant. They were extremely soft.

The CdI_2 crystals are known to possess hexagonal symmetry. The X-ray diffraction study of the dendritic crystals has revealed that the two faces of a dendrite,

through very rough in appearance and irregular in shape, lie parallel to *ab*-planes, such that the stem of the dendrite is directed along *a* (or *b*) axis. Further, the X-ray diffraction has shown that within a dendrite the arms, the secondary arms and the stem are crystallographically similarly oriented, i.e., they all have common directions of *a*, *b* and *c*-axes, irrespective of their positions in the dendrite. Therefore, the different portions of a dendrite do not require separate settings for obtaining their respective X-ray photographs.

The information gathered from the oscillation photographs has been put in a tabular form (Table I).

Fig 3 A full dendrite. optical micrograph: × 25

Table I

Information gathered from the X-ray photographs of the dendrites

Starting material; Growth chamber atmosphere	No. of X-ray photographs taken	Polytypes observed	No. of cases of streaking	No. of cases of arcing
Analar grade; Argon	46	4H : 41(89%) 4H + 12R : 1(2%) 4H + higher (Unidentified): 4(9%)	4(9%)	19(41%)
Zone refined; Argon	39	4H : 37(95%) 4H + Higher (Unidentified): 2(5%)	2(5%)	9(23%)
Zone refined; Vacuum	57	4H : 57(100%)	NIL	7(12%)

The most striking feature seen in the table is that out of 142 X-ray diffraction photographs, as many as 135 have only displayed reflections of the polytype 4H, which is known to be the most stable structure of cadmium iodine, both at room temperature and at higher temperatures. In the crystals grown in vacuum with high purity material, the occurrence of 4H is cent percent. This is in sharp contrast with the earlier results obtained for CdI_2 hexagonal plates grown from vapour in a very similar way[8], where the occurrence of higher polytypes had been found to be quite frequent. The discrepancy may be attributed to the difference of temperature of crystal growth in the two cases. For the growth of hexagonal plate-shaped crystals, a temperature of 360°C was used at the charge and the crystals grew in a temperature range around 100°C. In the present case of dendritic growth, the temperature at charge has been around 500°C and in the region of crystal growth, around 300°C (the m.p. of CdI_2 is 388°C). Since 4H is known to be the only stable high temperature modification of CdI_2, at such high temperatures the growth of this modification alone can be expected. Through earlier extensive studies of solid state phase transformations in the CdI_2 crystals upon heating, it has been well established that at high temperatures all polytypes transform into 4H[9].

Fig 4 X-ray a-axis 15°-oscillation photograph of a dendritic single crystal showing streaking; camera radius 3 cm; CuK_α radiation; polytype 4H; × 1.7

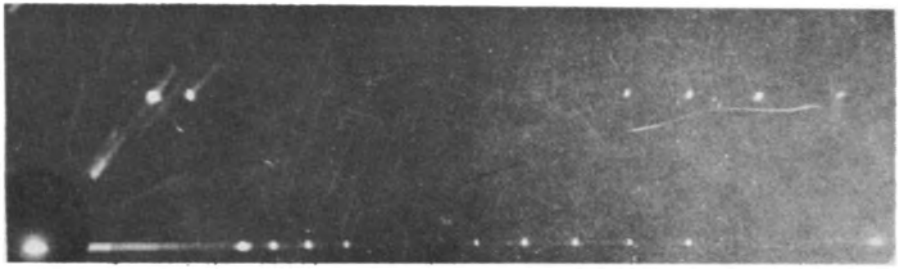

Fig 5 X-ray a-axis 15°-oscillation photograph of a dendritic single crystal showing reflections of normal 4H polytype; other conditions same as in Fig 4

Further, from Table I it is seen that the purification of CdI_2 leads to increase in percentage occurrence of the 4H structure. For crystal growth in argon atmosphere, when analar grade CdI_2 is replaced by the highly pure zone refined material, the occurrence of 4H rises from 89% to 95%. Next, the replacement of argon atmosphere by vacuum raises the occurrence of 4H from 95% to 100%. It follows that the impurities present in the material and in the atmosphere of the growth chamber are solely responsible for the formation of polytypes in the crystals.

The observed streaking in the X-ray photographs consists of successive reflections running into one another through streaks of varying intensities. An example is shown in Fig. 4, which may be compared with Fig. 5, depicting the X-ray photograph of a normal 4H polytype. The streaking arises from the presence of random stacking faults in the structure[10]. The phenomenon of arcing consists of extension of reflections on a X-ray photograph into small arcs, made up of two or more spots. An example is shown in Fig. 6. It results from the movement of edge dislocations into small-angle grain boundaries which then divide a crystal into two or more mutually tilted blocks[10]. Table I also reveals a regular change in the per-

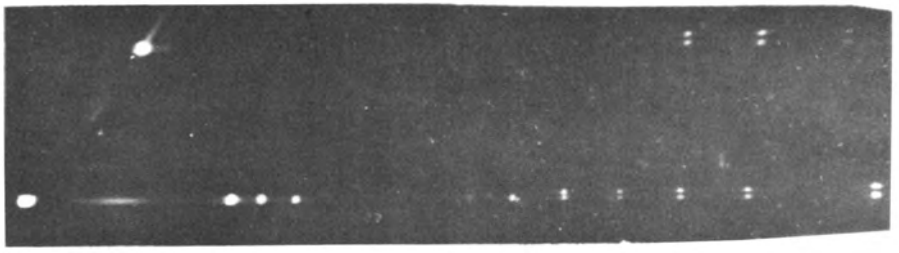

Fig 6 X-ray a-axis 15°-oscillation photograph of a dendritic single crystal showing arcing; other conditions same as in Fig. 4

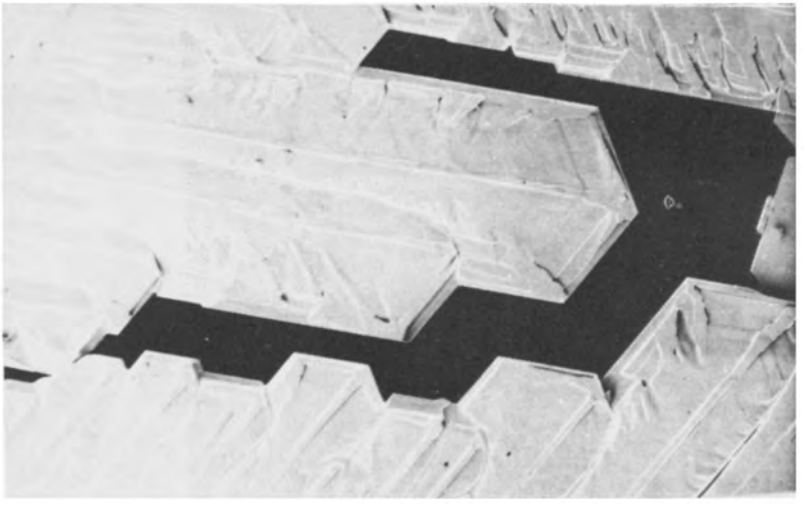

Fig 7 Scanning electron micrograph showing hexagonal terminals of primary and secondary arms of dendritic single crystals; 5kV; × 200

centage occurrence of streaking and arcing for the dendrites grown from materials of different purities and in different atmospheres. When analar grade CdI_2 is replaced by zone-refined CdI_2, for crystals grown in argon atmosphere the occurrence of streaking is reduced from 9% to 5%. Similarly, the arcing goes down from 41% to 23%. This clearly establishes the effect of impurity content on (*i*) one-dimensional disorder inside the crytal and (*ii*) formation of tilt boundaries in the

crystals. When argon atmosphere is replaced by vacuum, their occurrences are further reduced to nil and 12%, respectively. It implies that the impurities present in the argon gas also affect the production of edge dislocations in the crystals, which are basically responsible for the observed phenomena of streaking and arcing.

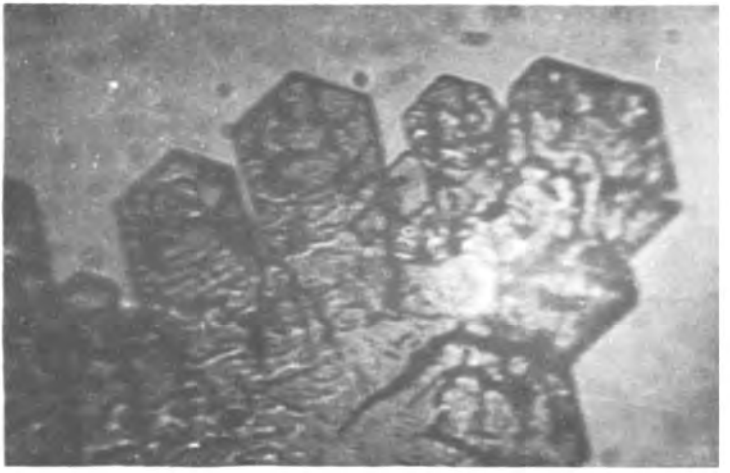

Fig 8 Optical micrograph showing hexagonality of tips of dendritic single crystal; × 160

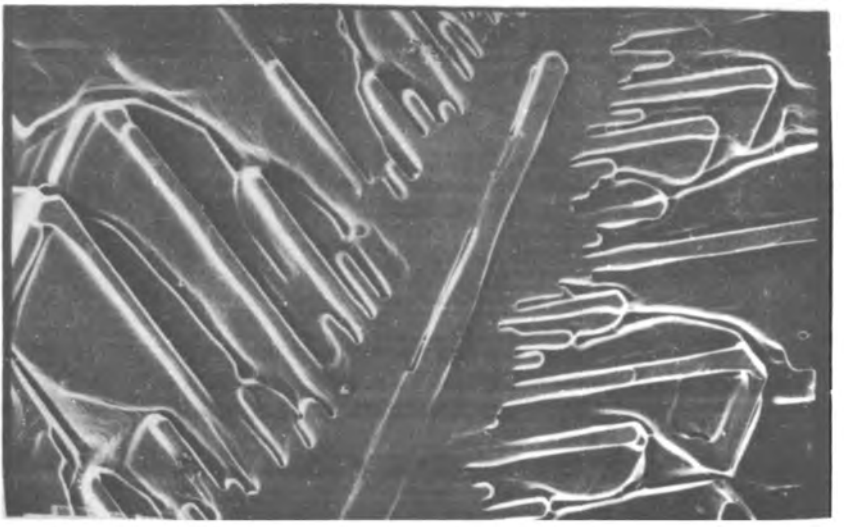

Fig 9 Some typical growth features observed in most of the dendrites: scanning electron micrograph; 5kV; × 500

Microscopic observations of the crystals have revealed that the arms and other parts of the dendrite have hexagonal edges (Figs 7 & 8). Figs. 9 and 10 show typical dendritic growth features. Fig. 11 is a magnified version of a small portion of Fig. 10. It shows the hexagonal shape of the steps which is in conformity with the hexagonal symmetry of the CdI_2 crystals.

Fig 10 Additional typical growth features observed in most of the dendrites; scanning electron micrograph; 5kV; ×400

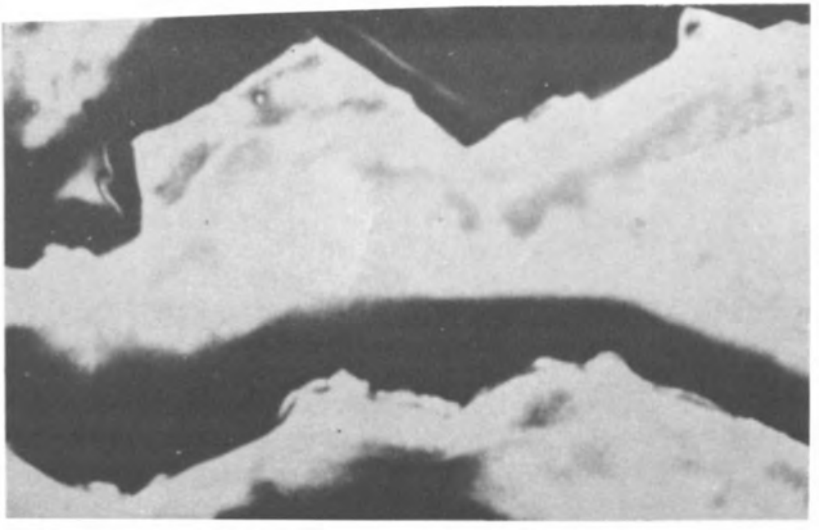

Fig 11 Magnified picture of a small portion of Fig. 10 showing haxagonal shape of growth steps; scanning electron micrograph; 5kV; × 7,000

Some dendrites have shown features of layer growth mechanism. No growth spirals have been observed on the dendrites. Further work is under progress.

Acknowledgements

Binay Kumar expresses his gratitude to Shri K Singh, N Shukla, S Mehdi and M Saha for helpful discussions and to Shri S Saxena for help in fabricating the crystals growth set-up. He is indebted to the UGC, India, for financial support.

References

1 F Weinberg and B Chalmers *Canad J Phys* **29** (1951) 382
2 A Papapetrou *Z Krist* **92** (1935) 89
3 W Wrangler *Acta Chem Scand* **9** (1955) 661
4 G C Trigunayat A survey fo the phenomenon of polytypism in crystals *Solid State Ionics* (*to be published*)
5 G C Trigunayat *Phase Trans* **16/17** (1989) 509
6 S K Chaudhary and G C Trigunayat *J Cryst Growth* **57** (1982) 558
7 G C Trigunayat and G K Chandha *J pure appl Phys* **2** (1964) 392
8 G K Chadha *Ph D Thesis* University of Delhi (1967)
9 G Lal and G C Trigunayat *J Cryst Growth* **11** (1971) 177
10 G C Trigunayat *Nature* **212** (1966) 808